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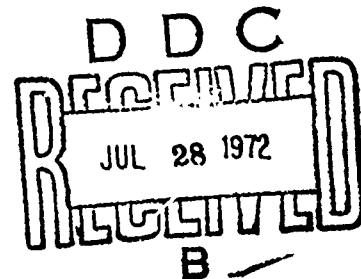


**POLYMER AND POLYMER-BITUMEN MATERIALS FOR
PROTECTING PIPELINES FROM CORROSION**

By

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Country: USSR



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13. ABSTRACT The VNIIST has developed an epoxy-coal-tar composition which has the properties necessary for coating large-diameter gas pipelines: ability to be hardened by hot or cold methods, mechanical stability, chemical stability, reasonable cost, good adhesion, long service life, stability over a wide temperature range. The book discusses: raw materials for polymer and polymer-bitumen coatings; rubber-bitumen and polymer-bitumen insulating materials (brizol wrapping, bitudiene, bitulene, bitumen-polydiene-polypropylene enamel); coatings based on synthetic resins; techniques for preparing and applying coatings under factory and field conditions. 49 figures; 48 tables; 67 bibliographic citations.			

I

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This book sets forth the nomenclature and characteristics of insulating materials used to protect pipelines from corrosion, as well as the mechanical and protective properties of these materials; methods for obtaining and applying such coatings and for standardizing them are also considered. The book describes ways of formulating various insulating coatings, equipment and techniques for obtaining the newest insulating materials and coatings and applying them to internal and external pipe surfaces under factory and field conditions, and the principal methods for testing insulating materials and coatings.

This book is intended for engineering and technical personnel involved in the fabrication and maintenance of pipelines.

INTRODUCTION

The proliferation of main pipelines and a significant increase in pipe diameters, along with the installation of pipelines in regions of the country with widely varying soil and climatological conditions, are imposing new, more stringent requirements on the quality of anti-corrosion coatings and the means for applying them.

Losses of structural metal, and expenditures for metal protection, are heavy in a number of countries; in the United States losses ran 5.4 billion dollars in 1949, and 8 billion dollars in 1956. In England annual corrosion-related expenditures for the same period amounted to 600 million pounds sterling (1.68 billion dollars), and in Austria and Canada they came to 100 and 300 million pounds.

According to data which are far from complete, a significant proportion of the total ferrous metals consumed by industry and our country's national economy is going into the replacement of losses caused by corrosion. Moreover, it is difficult to estimate the losses due to leakage and evaporation of valuable products, and the expense involved in down time when equipment breaks through and must be repaired.

In the 1930's and 1940's the USSR made widespread use of petroleum derivative coatings with kaolin as the mineral filler. Such coatings did not provide long-term protection of the pipelines under operating conditions: their average service life was limited to eight to twelve years.

Since the 1950's the insulation used to protect pipelines from corrosion has been a combination of rubber-bitumen enamel and a rolled rubber-bitumen material known as brizol (at the present time fiberglas is for the most part used as the wrapping material). Rubber-bitumen insulation provides long pipeline service life. It can be applied by mechanical methods, and can be used under widely varying soil and climatological conditions.

In recent years much has been done in the USSR to improve bitumen construction materials containing rubber. Differing opinions have been expressed with regard to combining pulverized rubber with bitumens. Several investigators have noted that the light oils contained in asphalt are slowly absorbed by the rubber, making it swell. Other authors believe that rubber based on natural rubber has a greater effect on the properties of bitumen.

According to one point of view, in order to obtain the desired effect from adding rubber, the rubber should be completely dissolved in the bitumen. Another theory is that the rubber is only partially dissolved when added to the bitumen, and thus the viscosity of the system is increased.

An opinion also exists that the pulverized rubber, depending on the degree of vulcanization, the presence of non-rubber components, and the method of combination, behaves like a highly polymerized substance in the mixture. Our own opinion is that the degree of swelling and dispersion is the result of the action of the whole bitumen as such, and not of any one component --the malthene fraction. According to this point of view, the rubber and bitumen composition is a unique colloidal mixture of rubber (polymer) in molten bitumen containing components with a low molecular weight.

Some investigators believe that when the rubber is introduced into, for example, asphalt concrete, it retains all the properties of vulcanized rubber. Rubber must be introduced in large quantities if it is to impart any of the properties of rubber to the coating. It is believed that vulcanized rubber cannot be dissolved in bitumen, since it contains too few hydrocarbons capable of penetrating into the structure of the rubber. This assertion is unfounded, and has been refuted by research.

Low-molecular-weight substances (plasticizers) act differently on polymers: they can be suitable with respect to some, and not very suitable with respect to others. The viscosity of the mixtures depends in significant measure upon the viscosity of the plasticizer used: plasticizers dissolved in the polymer form a system with a lowered softening point; they change the mechanical characteristics of the mixture. This makes it possible to adjust the composition of polymers.

Plasticization takes on special significance in a rubber-bitumen system. As rubber is introduced into bitumen it swells and is partially destroyed.

Consequently, bitumen plays the role of a plasticizer for the given polymer (rubber). When bitumen is combined with rubber, the latter lowers the brittleness temperature of the composition, increases its viscosity, and improves its elastic and plastic properties. Mutual plasticization can be assumed to occur in a rubber-bitumen system; this conclusion follows from actual production work with rubber-bitumen insulating materials.

Progress in the manufacture of new polymers makes it possible to use them for improving the mechanical properties of brizol mixtures and bitumen compositions.

At the present time rubber-bitumen insulation is widely used in the laying of major pipelines to protect them from soil corrosion.

Stepping up production processes, using high pressures, increasing flow rate of the product through the pipeline, and also operating pipelines and equipment under various soil and climatological conditions all require the development of more effective means of protecting pipelines from the complex interactions of corrosion factors.

In the early 1960's mixtures of bitumen coatings with polymers were developed and successfully introduced: polyethylene, polystyrene, polypropylene, polydiene, and others. Varying the qualitative composition of polymers and the method of combining them with bitumen makes it possible to obtain polymer-bitumen compositions with varied properties.

Now qualitatively new coatings have been developed from polymer resins (of the type of epoxy compositions without solvents), and they have a number of advantages over compounds containing solvents (negligible shrinkage, high density with few pinholes and capillaries, high chemical stability and longevity). Research has shown that polymer resins can be hardened by a cold method. The necessary thicknesses of the protective coating are attained with one or two applications of the insulating layer, which cuts expenses significantly in comparison with paint and varnish coverings, with which a protective layer is obtained only after eight to ten coats.

With the passage of time there has been great progress in protecting the external surfaces of pipelines from soil corrosion, both in our country and abroad. Pipelines are no longer laid in the ground unless they are insulated. In recent years interest has also arisen in internal protection of pipelines. Internal insulating coatings protect the pipeline walls from various corrosive agents, help decrease friction at the product-metal boundary during pumping, prevent paraffin deposition in the pipeline, and prevent contamination of liquids pumped through the pipeline and formation of residues in the pipeline.

Synthetic resins and plastic compounds are more used at the present time for protection of pipelines from corrosion. The world production (excluding the USSR) of the basic synthetic materials (resins, plastic compounds, chemical fibers, synthetic rubbers) has exceeded 15 million tons, a large proportion of it consisting of resins and plastic compounds.

Compositions based on epoxy resins have come into practical use in the prevention of corrosion. Their high dielectric properties, chemical stability in many corrosive media, low shrinkage, cold hardening capability, and good compatibility with other resins all ensure them wide application in the technology of protecting structures, pipelines and equipment from corrosion. The chemical properties of epoxy resins enable them to be modified; therefore in recent years various modified products have been used in the USSR and abroad to obtain protective coatings, instead of pure epoxy resin. Thiokol, polyamides, monoepoxides, coal tar, and others are among the active modifications.

In the United States, Federal Republic of Germany, and Japan epoxy tar compositions are also used for protective coatings for pipelines. The insulating coating used in the United States is composed of epoxy resin and a medium-oil fraction obtained from distillation of coal tar at a temperature of 270°C. Filler or pigment can be added to this mixture. The mixture hardens at room temperature with the addition of a semi-functional amine fast-hardening agent (ethylenediamine, ethylenetriamine, phenyldiethylamine, and others).

In Austria an insulating coating is used which is made from epoxy resin based on a glycidated ester, and coal tar prepared from commercial cresol, characterized by a boiling point of 230°C, and with catalysts containing diethylene-tri-oxin, triethylenetetramine and polyamide. Aromatic hydrocarbons, hydrogenated oils, ketones and esters, etc., are used as solvents.

In England an anti-corrosion enamel has been developed containing epoxy resin (bisphenol-epichlorohydrin, hydroxyphenyl) in amounts of 31 - 43.5%, aromatic hydrocarbons in amounts of 12.7 - 21.9%, coal tar in amounts of 32.5 - 49.5%, and filler -- talc, mica, clay -- in amounts of 12.7 - 17%.

An anti-corrosion coating used in the USSR is an epoxy lacquer obtained by dissolving epoxy resin (E-40, E-41, E-33) at 30 - 40°C in monomeric glycidated esters. An equivalent amount of polyamide is introduced into this solution. The lacquers obtained have a viscosity suiting them for application by spraying, immersion, pouring, and brushing. Lacquer films harden at 120°C. Polyamides incorporated into the composition of lacquers act as hardeners for the epoxy resin.

As a result of its research the VNIIST has developed an epoxy-coal tar composition which is applied by the spray method, by means of a specially developed sprayer or sprayer-mixer. This coating (without solvents) is presently being adopted for the insulation of large-diameter pipes. The chemical stability of the epoxy-coal tar compositions enables them to be used for insulating both internal and external surfaces of oil industry pipes and pipelines.

The protective effectiveness of insulating coatings is determined by their mechanical and chemical properties and by the conditions under which they are used, and also by the projected service life. The basic purpose of a protective coating is to totally insulate metal parts from the surrounding medium. A protective coating must be continuous, and contain no pinholes through which the surrounding medium can penetrate to the structural metal. The coating should have good adhesion, a hydrophobic nature, impermeability, and chemical resistance to various corrosive media.

Pipeline coatings are subjected to a variety of mechanical stresses (shearing, impact, flexure, friction, etc.). Thus the coating should be mechanically stable, to avoid perforation by the earth and damage during laying of the pipeline, and it should maintain its physical properties over a wide range of temperatures in the surrounding medium; it should be durable.

Coatings should not: be altered appreciably under pipeline operation conditions, or lose any of their physical, chemical, structural or mechanical properties when located in corrosive media. It is also important that a coating not contain any corrosive substances to act on the structural metal to be protected. Moreover, economy is an important requirement of anti-corrosion coatings for pipelines and other structures.

The epoxy-coal tar insulation developed at the VNIIST meets these requirements.

A. M. Zinevich, S. K. Noskov, N. G. Ryabchinkova, T. A. Radushnova, A. M. Aleksandrova, V. V. Egorova, and S. M. Kudryashova participated in developing techniques and methods for obtaining anti-corrosion materials and coatings, and in laboratory research. The author thanks these colleagues for their assistance in preparing materials for this book.

CHAPTER ONE

RAW MATERIALS FOR POLYMER AND POLYMER-BITUMEN COATINGS

The basic ingredients for producing polymer-bitumen and polymer insulating coatings are bitumens and polymers, including synthetic resins, hardeners, fillers and plasticizers.

Bitumens

Bitumens are mixtures of large numbers of hydrocarbons of varying molecular weights. Highly oxidized oil bitumens (OB) are usually used in the production of insulating materials --type IV and V structural (GOST 6617-56 or insulating (GOST 9812-61). Unlike structural bitumens, insulating bitumens have enhanced elastic and plastic properties, and are classified as winter or summer.

TABLE 1. PROPERTIES OF TYPE IV BITUMEN FROM VARIOUS FACTORIES

Factory-Supplier	Sulfur content in %	Depth of needle penetration in 0.1 mm at temperature in °C					% paraffin content	Brittleness temp. in °C
		+25	0	-5	-10	-20		
Orskiy	1.74	40	9	6	4	2	3.75	-10
Syzranskiy	2.82	20	5	4	2	1	7.51	+5
Novokuybyshevskiy	2.82	17	3	2	1	0	4.41	0
Lyuberetskiy	2.94	16	6	1	0.5	0	5.21	+5
Odesskiy	0.74	18	-	5	2	2	5.67	+5
Drogobychskiy	3.33	33	5	3	1	1	5.67	-

Oil bitumens are obtained from heavy oils by distillation of the butyric fractions or oxidation of the asphalt (petroleum distillation residue) in air at high temperatures. The oxidation process is accompanied by concentration

of resins and an increased quantity of asphalts and asphalt acids (Fig. 1); for example, type BN-V contains about 3% asphalt acids, and type BN-IV not more than 2 - 2.5%.

TABLE 2. ADHESION OF TYPE IV BITUMEN TO METAL AT VARIOUS SULFUR AND PARAFFIN CONTENTS

Factory-Supplier	Temperature in °C		Adhesion under a pull in kG/cm ²	Content in % of	
	pipeline application	adhesion determination		Sulfur	Paraffin
Lyuberetskiy	-20	+20	2.5	2.94	5.21
	+20	+20	5.6	2.94	5.21
Odesskiy	-20	+20	3.3	0.74	5.67
	+20	+20	6	0.74	5.67
Orskiy	-20	+20	4.5	1.74	3.75
	+20	+20	6	1.74	3.75



Fig. 1. Micelles of bitumen enamel.
1 - oils; 2 - resins; 3 - asphaltenes

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The physical and mechanical properties of bitumens (Tables 1 and 2) play an important role in manufacturing enamels for the protection of pipelines from soil corrosion. These properties depend on the oil, resin, asphaltene, sulfur and paraffin contents of bitumens. For example, oils and resins improve the elastic and plastic properties of bitumens, especially in the below-zero temperature range; increasing the asphaltene, carbene and carboïd contents of bitumens makes them tougher. The sulfur and paraffin contents of bitumens govern brittleness; bitumens become brittle when their sulfur content exceeds 2% (Table 3).

TABLE 3. BASIC PHYSICAL PROPERTIES OF STRUCTURAL OIL BITUMENS (GOST 6617-56)

Property	Standard specifications by type		
	BN-IV	BN-V	BN-VK
Penetration depth at 25° C in 0.1 mm, within limits of	21 - 40	5 - 20	Not below 20
Elongation at 25° C in cm, not less than	3	1	Not standardized
Softening point in °C, not below	70	90	90
Solubility in chloroform or benzene in %, not less than	99	99	99
Weight loss at 160° C over 5 hours in %, not more than	1	1	1

Bitumen-to-metal adhesion also depends on the chemical composition of bitumen: adhesion increases with increased asphaltogenic acids, and decreases significantly with an increase in paraffin content (more than 4%) (Table 4).

Insulating bitumens are used to protect pipelines under widely varying soil and climatological conditions. They should therefore be thermally stable in the summertime, particularly in southern regions of the country, and, on the other hand, they should be pliable at temperatures below zero, for insulating a pipeline which is to carry a product with a temperature of 50 - 80°C. Coatings should have good mechanical stability, adhesion to metal, and water repellency and chemical stability under a variety of soil conditions. Also of great significance is the durability of bitumens, i.e. their ability to maintain their original physical, mechanical and chemical properties for an extended period of time.

Other very important characteristics of insulating bitumens are the electrical insulating properties of bitumen coatings. In the initial state at 20°C insulating bitumens have a resistivity of 10^{15} ohms · cm, a dielectric constant of 2.5 - 3.5, and a breakdown voltage of 130 - 160 kv at a thickness of the material of 10 mm. It should be kept in mind that when the pipelines actually go into operation, the resistivities of bitumen coatings are decreased by several orders of magnitude. The main reason for lowering the resistivity of a bitumen insulating coating is its water-saturability in interactions with soil electrolytes.

Synthetic Resins

In recent years coatings made of synthetic resins --epoxy, polyester and furfuran-- have been coming into use for protecting pipelines and other structures from corrosion.

TABLE 4. BASIC PHYSICAL PROPERTIES OF INSULATING OIL BITUMENS (GOST 9812-61)

Property	Bitumen type		
	BN-I-IV	BN-I-2-IV	BN-I-V
Needle penetration depth at 25°C within limits of	25 - 40	30 - 40	Not less than 20
Elongation at 25°C in cm, not less than	4	4	2
Temperature in °C, not below: Softening Flash point	75	65 - 75 230	90
Solubility in chloroform or benzene in %, not less than		99	
Weight loss during 5 hours at 160°C in %, not more than		1	
Water-saturability over 24 hours in %, not more than		0.2	
Percent content:			
Water-soluble compounds, not more than		0.2	
Asphaltogenic acids, not less than		1.25	
Paraffin, not more than	-	4	-
Sulfur, not more than	-	2	-
Moisture		traces	

Furfuran resins are formed by the action of mineral acids upon a mixture of furfural and furfuran alcohol. These resins are easily hardened by acids with the formation of stable polymers. The most widely used are sulfonic acids (for example, benzene sulfonic acid).

Temperature has a tremendous effect on the rate of hardening: at ordinary temperatures furfuran resins take 24 hours to harden, and at higher temperatures (80 - 130°C) hardening time is cut to several hours. The furfuran resins mix well with various fillers: carbon black, graphite, coke, etc. This makes it possible to obtain insulating coatings with increased stability. Among the shortcomings of furfuran resins are brittleness, insufficient elasticity, and low adhesion to certain materials, particularly metals. If furfural, formaldehyde or phenol is added to the furfuran alcohol as it is heated, a modified resin is obtained which has better adhesive properties after hardening.

Furfuran resins are used as anti-corrosion lacquers, for example: furfural-acetone resin with fillers, hardened by sulfonic acid, is used as a coating for wood and metal; resins modified by polyamides, or natural or butadiene-styrol rubbers are used for protective staining of chemical equipment and structural items, pumping apparatus for sea water and solutions of certain acids, and in the construction of metal scaffolding and roofs of buildings.

Furfuran-resin-based products and their modifications are accepted industrially and are manufactured in the form of alcohol-acetone or alcohol-ethyl-acetate solutions (e.g. FL-2, FL-2L, FL-1, FL-4, F-10 and other lacquers). All coatings based on modified furfuran resins have anti-corrosion characteristics.

Polyester resins are obtained by condensation polymerization reaction of polybasic acids with polyhydric alcohols.

Unsaturated polyesters are very important in the manufacture of plastics; they are oligo (i.e., comparatively low-molecular-weight) products of condensation polymerization of di- or polyfunctional acids and alcohols containing double bonds.

Several types of polyester maleinates are produced by Soviet industry: PN-1 (STU-30-14086-63); PN-3 (VTU LSNKH-33122-60); PN-1S (STU-30-12039-61); PN-4 (VTU-P-220-60 LSNKH).

Polyester acrylates are products of the esterification of polyatomic alcohols, or of esterification of products of their condensation with dibasic or monobasic (meta-acrylic or acrylic) acids.

In appearance polyester acrylates are more or less viscous liquids, yellow to dark-brown in color, which can be made into tough products by starters and accelerators. In certain instances a monomer (methyl methacrylate) is added to them, which promotes cross-linking of the molecules.

A number of polyester acrylates are manufactured industrially: TGM-3 (VTU-BU-17-56); MGF-9 (VTU-BU-17-56); TMG-F-11.

Polyester maleinates and polyester acrylates usually contain styrol and other volatile monomers representing comonomer components, respectively, of 30%, 35%, and 10 - 25%.

Resins which are mixtures of polyester maleinates and polyester acrylates are also used. For example, the resin MA-3 (VTU-30-12044-61 LSNKH) is a homogeneous solution of type MS-1 ethylene glycol maleinate phthalate resin in a mixture of MGF-9 and TGM-3 polyester acrylates, with a density of 1.16 - 1.19 g/cm³, a viscosity (in VZ-4) of 60 - 140 seconds, and a hardening time of about 4 - 15 hours with 3% hydroperoxide of isopropylbenzene and 4% cobalt napthenate in styrol.

The polyester resins combine well with various organic and mineral fillers. Introducing a filler lowers the cost of the material, and makes it possible to minimize the effect of shrinkage. Fibrous fillers significantly improve the resilience and stability of hard compounds. Polyester compounds surpass epoxy and furfuran resins in resistance to oxidizing agents; however, increasing the ambient temperature seriously impairs the stability of polyesters.

A preponderance of the polyester resins manufactured goes into the production of clear plastics. Polyester resins are used as anti-corrosion coatings.

In a number of countries efforts have begun toward the application of polyester coatings on the internal surfaces of reinforced concrete pipes. The pipes acquire high chemical stability and gas impermeability, and are used instead of pipes made of non-ferrous metals. The compound is applied centrifugally or by means of a propeller sprayer advanced through the pipe. According to data from the Federal Republic of Germany, a tube with a diameter of 600 mm and a length of 1.5 m can be treated in 2 minutes.

The term "epoxy resin" refers to a large number of compounds with molecular weights from a few hundred up to several thousand. Epoxy resins are characterized by their number of epoxy groups, and their ability, under certain conditions, to be converted to infusible, insoluble polymers in the presence of hardening substances.

Only the so-called diene epoxy resins are presently manufactured on an industrial scale; the initial product for their synthesis is diphenylpropane or diene. The diene epoxy resins are the products of condensation of epichlorohydrin and diphenylpropane in an alkaline medium. A polymer product is formed as a result of the hardening of epoxy resins. Hardened epoxy resins possess high stability and dielectric properties, good adhesion to metals and other materials, and good photo-stability and chemical stability.

TABLE 5. BASIC PROPERTIES AND REQUIREMENTS

Property	Technical specifications	Experimental results
External appearance	Low-viscosity resin, light-yellow to brown in color	Low-viscosity, light-brown in color
% content		
epoxy groups	Not less than 22	25.5
volatiles at 120°C	Not more than 2.5	1.32
bound chlorine	" " 2.5	1.2
Viscosity in centipoise	" " 80	24

The main trend in the use of epoxy resins is for insulating coatings; a large proportion of the epoxy resins produced annually goes for this purpose.

Economical protective coatings for buried pipelines based on epoxy and coal tar resins are in use in England, the Federal Republic of Germany, Japan and the United States.

Admixtures of coal tar resin, pitches and bitumens to the resin can go to 200% or higher. Mixtures used for coatings contain varying proportions of quartz or apatite filler (up to 70% of the mixture by weight).

The disadvantage of using epoxy-coal tar compositions lies in the fact that they are inferior to unmodified epoxy compounds in thermal stability and resistance to the action of solvents and acids. However, in many specific instances they seem to be adequate in these respects.

TABLE 6. BASIC REQUIREMENTS FOR EPOXY RESINS

Properties	Type of resin				
	ED-6	ED-P	ED-L	ED-37	E-40
Density in g/cm ³	1.2 - 1.3				
% content:					
epoxy groups	14 - 18	11 - 14	8 - 11	11 - 17	14 - 20
volatiles, not more than	1	1	1	6.5	8
Viscosity in sec, not more than:					
resins without hardener at 50°C	100				
resins without hardener at 100°C (within 2 hours after mixing)	20	35	100	-	-
Molecular weight	450-600	600-750	750-1000	-	-

Various thinners are used with the commonly used solvents to adjust the viscosity of epoxy coal tar compositions. Mono-epoxies are used as thinners, for example certain aliphatic epoxy resins (AER) developed and adopted by industry in recent years. These resins improve the elasticity, thermal stability and dielectric properties of the compositions. Table 5 shows the main properties of type DEG-1 (or TEG-1) aliphatic epoxy resins (STU No. 30 12402-62).

Epoxy resins of various types are currently being manufactured (GOST 10587-63): ED-5, ED-6, ED-P, ED-L, E-37 (STU-30-14112-63), E-40, E-41, F-44, E-181.

Table 6 shows the basic requirements for manufactured epoxy resins.

ED-5 type resin is most widely used for insulation. Its basic properties are listed below.

Content of epoxy groups	18 and more
Content of volatiles in %, not more than	2
Viscosity of resin in sec, not more than:	
without hardener at 25°C	75
with hardener at 100°C within 2 hours after mixing	10
Molecular weight	370 - 450
Density in g/cm ³	1.2 - 1.25
Dissociation temperature in °C	340 - 350
Coefficient of linear expansion	4.5 - 5.5 · 10 ⁻⁵
Coefficient of thermal conductivity in kcal/m · hr × × degrees	0.17
Dielectric permeability	3.5 - 4.2

Dielectric loss tangent:	
at 20°C	0.001 - 0.002
at 80°C	0.03 - 0.05
after 48 hours in water at 20°C	0.001 - 0.003
Specific volume resistivity in ohm · cm:	
at 20°C	10 ¹⁵
at 80°C	10 ¹¹
after 48 hours in water at 20°C	10 ¹⁴
Breakdown voltage in kv/mm	25 - 30

Plasticizers

In order to increase the plasticity and elasticity of a composition, for instance, for operation under winter conditions, plasticizers are incorporated into it which, depending on the amount introduced, lower the softening point of the enamel to a greater or lesser degree.

The plasticizers considered most effective are those which cause the least impairment of structural and mechanical properties as they impart elastic and plastic properties to the composition.

The main plasticizers for bituminous insulating coatings are the petroleum oils: green, transformer, axle, spindle, automotive; polymers --polyisobutylene, solution of polyisobutylene with green oil, low-density polyethylene; low-molecular-weight synthetic rubbers --polydiene, SKD-ZH and SKSP-ZORPZH and octol.

Transformer oil (GOST 982-56) is obtained from products of the distillation of petroleum by sulfuric acid refining. Its properties are given below.

Color	light-yellow
Density in g/cm ³	0.87
Kinematic viscosity in centistokes:	
at 20°C	30
at 50°C	9.6
Acid number in mg KOH per 1 g of substance	0.05
Formation of water-soluble acids during the curing process in mg KOH per 1 g substance:	
non-volatile	0.005
volatile	0.005
Stability:	
residue after oxidation in %	0.1
acid number after oxidation in mg KOH per 1 g substance	0.35
ash content in %	0.005
Temperature in °C:	
flash	135
gel	45
Sodium sample with acidification	2 points
Transparency at 5°C	Transparent

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Polyisobutylene (TU MKHP-1665-54). The molecular weight of polyisobutylene ranges from 8000 to 200,000. It occurs in various physical states from viscous-fluid to hard-elastic, depending on the molecular weight. Polyisobutylene is distinguished by its low glass point (-74°C); in its properties it is reminiscent of rubber, but, being a saturated polymer, it cannot be vulcanized. It is used principally as a plasticizer.

A 5% colloidal solution of type P-200 polyisobutylene in green oil is also used as a plasticizer. For this purpose granulated polyisobutylene is flooded by green oil level with the mass of the polyisobutylene. According to the degree of its swelling, green oil is added up to the amount computed. Mixing continues until the mixture assumes a jelly-like consistency.

Polydiene is a by-product of the manufacture of synthetic rubber; it has a flash point no lower than 145°C , a viscosity of 28 poise, a moisture content of 0.2%, and a boiling point above 250°C .

Viscosity is sharply decreased with increased temperature (Fig. 2): at 100°C polydiene is in a state of mobile liquidity, with η falling from 3220 to 16 centistokes; after that viscosity drops slowly with an increase in temperature, and in the range from 100 to 150°C η varies from 16 to 5 centistokes.

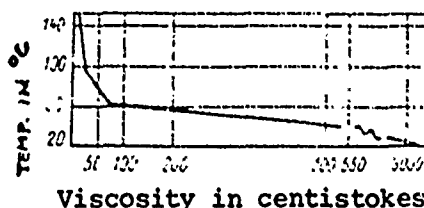


Fig. 2. Dependence of viscosity of polydiene on temperature

SKD-ZH is a synthetic rubber which is divinyl, liquid, and dark-brown in color, with a viscosity of 30,000 centipoise. The molecular weight is about 10,000. There is no bound acid in the composition of SKD-ZH; the free acid content is 1.66%, and the ash content is 0.16%.

SKSP-30 RPZH is a synthetic rubber which is divinyl-styrol, liquid, light-brown in color, regulated, paraffinated, with a viscosity of 37,000 centipoise, and containing 30 parts by weight of styrol. The molecular weight is 16,000. It contains 0.06% bound acid, 2.7% free acid, 0.5% volatile substances, and 0.3% ash.

Ozocerite is a mineral wax which is a bituminous substance made up of a mixture of higher hydrocarbons of the paraffin series; its color is from yellow-brown to black, it has a faint petroleum odor, and it is a product of the natural distillation of oils with a paraffin base. It is found in the form of veins in regions of petroleum deposits, and in the form of small accumulations in coal seams. Ozocerite is manufactured in four grades: top, I, II and III. Table 8 gives its main properties.

Ozocerite composition (a mixture of ozocerite with paraffin) is made up of $45 \pm 5\%$ ozocerite and a commercial paraffin. Based on drop temperature, there are two types of ozocerite composition, 64 and 65. Their properties are shown in Table 9.

TABLE 8. TECHNICAL PROPERTIES OF OZOCERITES

Property	Grade of ozocerite			
	Top	I	II	III
Drop temperature in °C, not below	80	75	71	61
Needle penetration depth at 25°C and a load of 100 gram force/ /5 sec in 0.1 mm	25	35	35	70
% content:				
ceresin, not less than	78	75	70	65
physical impurities, not more than	1	1.5	1.5	2
moisture, not more than		0.5		

Ozocerite and ozocerite composition are used as a plasticizer and anti-oxidant in the manufacture of brizol. They improve the quality of the brizol fabric and lower its water-absorption. However, introducing these plasticizers also decreases the stability of brizol fabric; they are therefore added in amounts from 1 to 5%, as a rule.

TABLE 9. TECHNICAL PROPERTIES OF OZOCERITE COMPOSITIONS

Property	Type	
	64	65
Drop temperature in °C, not below	64	65
Needle penetration depth at 25°C and a load of 100 gram force/5 sec in 0.1 mm, no more than		40
% content of physical impurities, no more than		2

Green oil, a brownish-green, opalescent liquid, is a mixture of heavy products of a series of aromatic hydrocarbons with hydrocarbons of saturated and non-saturated series. It is obtained from the pyrolysis of raw petroleum, and is used in the printing and paint and varnish trades, and as a basic raw material in the manufacture of lampblack. Green oil is used as a plasticizer for butadiene styrol rubbers. In rubber-bitumen enamels, green oil is used as a plasticizer and antiseptic, increasing the resistance of the enamel to cold and to biological agents.

TECHNICAL PROPERTIES OF GREEN OIL

Fractional composition:

initial distillation temperature in °C no less than	150
no more than (in %) distilled up to 350°C	95
Coking capacity in %, no more than	0.75
% content, no more than:	
napthalene	8
moisture	traces

Octol (synthetic cable grease) is obtained by polymerizing isobutylene in the presence of a catalyst. Its basic technical properties are viscosity, acidity, and absence of free sulfur.

TECHNICAL PROPERTIES OF OCTOL

Density in g/cm ³	0.867
% content:	
chlorides and sulfides	traces
physical impurities	0.0344
Copper plate test	passes
Flash point in open crucible in °C	176
Acid number in mg KOH per 1 g substance	0.046
Kinematic viscosity at 100°C in sec	81.4

Introducing octol into rubber-bitumen enamels reduces their shrinkage and increases their resistance to cold.

Also used for plasticizers of synthetic resin coatings are coal tar and polyamide resins, thiokol, low-molecular-weight synthetic rubbers, and aliphatic epoxy resins.

Coal tar resin (GOST 4492-65) is a liquid of brownish-black color; the product of high-temperature coking of coal, it consists mainly of aromatic

TABLE 10. TECHNICAL PROPERTIES OF COAL TAR RESIN

Property	Type of resin		
	A	B	C
Density as converted to anhydrous resin at 20°C in g/cm ³	1.14 - 1.18	1.17 - 1.22	no more than 1.22
% content:			
moisture	3.5		4
substances not soluble in toluol, as converted to anhydrous resin, no more than	7		9
naphthalene	8	9	no more than 10
phenols	1.7	1	not normalized
% ash content converted to anhydrous resin, not more than	0.08	0.1	0.2
Arbitrary viscosity at 80°C in °C	not normalized		2.5 - 4.2
pH of water extraction, within limits	5 - 7		not normalized

hydrocarbons. Table 10 gives the basic properties for coal tar resin.

Thiokol, a dark, viscous liquid lacking cross-linkings, is a low-molecular-weight polysulfide polymer. It imparts the required plasticity to an epoxy-resin-based coating. Epoxy-thiokol compositions retain high stability factors better than other similar compounds at temperatures below 0°C. The molecular weight is 2000 to 3000. Table 11 shows the basic properties of thiokol.

TABLE 11. TECHNICAL PROPERTIES OF THIOKOL

Property	Type	
	T (MRTU 6-04.156-63)	FKH (MRTU 27/3-8-63)
Viscosity at 25°C in poise	247	187
% content:		
moisture	0.17	traces
hydrogen sulfide	2.59	-
sulfur	39.4	-
volatiles	0.05	-
insolubles	1.5	-
iron	0.0295	-
Time required for loss of tackiness of vulcanized thiokol in hours	22	20 - 12
Tensile strength in kg/cm ²	19	12 - 9
Elongation in %:		
relative	405	250
residual	8	8

In speaking of rubbers (natural or synthetic), it must be borne in mind that these terms (especially synthetic) refer to rubbers of different types, each exhibiting its own specific effect on the properties of bitumens.

The most interesting feature of combined rubber and bitumen is that a low proportion of rubber (0.1 - 1% of the weight of bitumen) can drastically alter the properties of the bitumen. If more than 3% rubber is added, the bitumen becomes rubber-like. If rubber is dispersed up to total solution in the bitumen, it has less effect on the properties of the bitumen.

Hardeners

In order to impart the necessary structural and mechanical properties to compositions based on thermo-setting resins, they are hardened. The presence of two types of functional groups in an epoxy resin makes it possible to harden it with various substances capable of interacting not only with epoxies, but also with hydroxyl groups. Depending on the type of hardening agent used, the hardening process can occur at room temperatures, accompanied by a considerable evolution of heat, or after heating. Poly-alcohols, amines, anhydrides of dicarboxylic acids, carboxylic acids, diisocyanates, diphenyls, various resins and certain other compounds are used as hardeners. Alcohols have not gained wide acceptance as hardening agents. Ethylene diamine, hexamethylene diamine, diethylene triamine, polyethylenepolyamine, and certain other amines are most generally used.

Polyamide resins L-18 and L-20 are widely used in the USSR. They are made on a linseed oil base; the amine number is about 100 HCl/g substance, and the viscosity is 10,000 centipoise.

TABLE 12. BASIC PHYSICAL PROPERTIES OF EPOXY RESINS WITH DIFFERENT HARDENERS

Property	ED-6 resin			ED-5 resin	
	+30% maleinic anhydride	+6.5% polyethylenepolyamide	+7% hexamethylene diamine	+10% polyamines	+40% maleic anhydride
Limit of stability during flexure in kg/cm^2	1000	1000	700	-	-
Specific impact viscosity in $\text{kg}\cdot\text{cm/cm}^2$	8.65	7.1	7	-	-
Brinell hardness in kg/mm^2	17.2	18.3	-	-	-
% water absorption	-	-	-	-	0.05
% shrinkage	-	-	-	0.5	up to 1
Dielectric permeability	4.1	4.3	4.85	-	-
Dielectric loss tangent at 10^6 hz	0.014	0.021	0.023	0.008	0.005
Volume resistivity in $\text{ohm}\cdot\text{cm}$	0.15×10^{15}	0.36×10^{15}	$3 \cdot 10^{15}$	$5 \cdot 10^{15}$	$1 \cdot 10^{15}$
Breakdown voltage in kv/mm	13.6	27.4	22	4.7	5

Depending on their structure, the polyamide resins usually contain primary, secondary, and in some cases also tertiary amino groups, and are therefore capable of reacting with epoxy resins. Polyamide-epoxy coatings have demonstrated high stability when tested in sea water for 24 months, and sufficient stability after three months in water, 5% sulfuric acid, benzene, and diesel oil.

Since they have two types of reactive groups, epoxy resins interact with phenol-, urea- and melamine-formaldehyde and furfuran resins, as well as with liquid polysulfide rubbers.

The most widely used hardener for epoxy resins is polyethylene polyamine (TU-Pl0-55), a mobile, light-yellow liquid. Research indicates that the hardener chosen exerts a significant effect on the physical and mechanical properties of hardened epoxy resins (Table 12).

diphenylhydrazine DFG (GOST 40-40) and paste No. 9 are vulcanizing agents for liquid thiokol. Paste No. 9 is composed of peroxides of manganese, dibutylphthalate and stearic acid. Hydroperoxide of isopropylbenzene (cumene) and napthenate of cobalt in the form of an 8 - 10% solution in styrene are used to harden polyester resins.

Compounds with acid properties used as hardeners determine the gradual nature of polymerization. The rates of such reactions are determined by the temperature of the surrounding medium and by the concentration of the hardener.

A whole series of hardeners is used to harden furfuran polymers: aniline hydrochloride and Petrov catalyst (note: equivalent of Twitchell reagent), paraphenylurethane-sulfochloride and ferric sulfate, parabenzene sulfonic acid and p-toluol sulfonic acid.

Benzene sulfonic acid best hardens a furfural-acetone monomer when it is introduced in an amount equalling from 10 to 30% of the weight of the monomer

Fillers

Fillers are incorporated into compounds to improve the physical and mechanical properties of compositions, decrease shrinkage during hardening, and lower the cost of coatings. They can be classified into two groups: fibrous and granulated. The basic requirements for fillers are fine particle size, low moisture-saturability, hydrophobic nature, and resistance to the action of various corrosive media.

The quantity of filler introduced depends on the particle size, wetting capability, and purpose of the material.

Granulated fillers come in a multitude of forms. They are classified into mineral (silica, chalk, talc, limestone, finely ground portland cement; and diabase, andesite, quartz, and granulated mica), and organic (granulated rubber from worn-out automobile tire treads, low-density polyethylene, carbon black, et al.). Talc, andesite flour, and granulated diabase, along with others, are usually used for coatings based on synthetic resins.

Most fibrous fillers used are asbestos ones. Fillers can be introduced into the poured mass or mold in large amounts (up to 200% of the weight of the composition), which significantly lowers the cost of the material.

Asbestos (GOST 7-70) is capable of being cracked into flexible, strong fibers. In chemical composition the majority of asbestos minerals are magnesium silicates, and some silicates of sodium and calcium. The combination of flexibility, thinness, and elasticity of asbestos fiber, along with its high mechanical stability, incombustibility, adsorptive activity, and in some cases high chemical stability as well, make its widespread use inevitable.

The asbestoses belong to two mineralogical groups: amphibole and chrysotile. Chrysotile asbestos is more generally used in industry. The fibers of chrysotile asbestos are more stable and elastic than those of most kinds of amphibole asbestoses.

Chrysotile asbestos is not an acid-resisting material: acids dissolve the magnesium contained in it, and the remaining silicon matrix is unstable, brittle, and easily crumbled into grains. In reactivity to alkalies, chrysotile asbestos is one of the most stable minerals.

Thermal stability --the ability to withstand high temperatures-- is an important characteristic of chrysotile asbestos. Asbestos is fireproof; however, high temperatures alter its physical properties: when heated to 700°C it loses water of constitution.

TECHNICAL PROPERTIES OF CHRYSOTILE ASBESTOS

Index of refraction	1.50 - 1.57
Density in g/cm ³	2.4 - 2.6
Melting point in °C	1500
Thermal stability in °C:	
under prolonged constant heating	550
under brief heating	700
Resistance to alkalies	High
Resistance to acids	Low
% moisture content no more than	3

Asbestos is used in the manufacture of rolled brizol fabric and rubber-bitumen enamels. An asbestos content of 8 - 12% increases the tensile strength of brizol up to 20 kg/cm². However, increasing the asbestos content above 15% makes the material brittle. Asbestos is introduced into rubber-bitumen enamels in a quantity of from 7 - 10%.

Pulverized rubber (TU SHU-96-56) is a product of the reprocessing of scrap auto tire treads from domestic industry. This is a multi-component combination containing a great number of ingredients, principal among which are rubber, anti-oxidants, fillers and a vulcanizing radical.

TECHNICAL PROPERTIES OF GRANULATED RUBBER

% content:	
textile, no more than	5
moisture, no more than	1.5
ferrous metals after magnetic scouring	0.1
Sieve opening in %, no less than:	
with an aperture of 1.5 mm	100
with an aperture of 1 mm	96

Table 13 shows the composition of rubber powder.

TABLE 13. COMPOSITION OF RUBBER POWDER

Constituents	Composition in % rubber	
	Whole tire	Tire tread
Rubber	50.9	55.2
Plasticizer	8	6
Carbon black	32	33
Zinc oxide	3.5	2.8
Sulfur	1.6	1.6
Textile fiber	4	1.4

Polyethylene. Polyethylene is one of the most valuable polymer materials. This relatively soft thermoplastic polymer has a crystalline structure similar to that of normal paraffins (for example, $C_{60}H_{122}$). In the absence of oxygen, polyethylene is stable up to $290^{\circ}C$. Between $290^{\circ}C$ - $350^{\circ}C$ it dissociates into low-molecular-weight, wax-type polymers, and above $350^{\circ}C$ into low-molecular-weight gaseous substances. At room temperature polyethylene is not soluble in any of the common solvents, and it is resistant to a number of acids, with the exception of fuming sulfuric and concentrated nitric acid, nitrating mixtures, and chromic acid. Under exposure to atmospheric oxygen, ultraviolet rays and heat, the physical, mechanical and dielectric properties of polyethylene progressively deteriorate. Polyethylene has high water-repellency and very low water-saturability. The average molecular weight of low-density polyethylene is 60,000 - 300,000.

The mechanical properties of polyethylene depend on its molecular weight; the higher the weight, the worse they are. Table 14 shows the main properties of polyethylene.

The decomposition of polyethylene begins at $200^{\circ}C$. When introduced into a brizol composition, polyethylene increases its stability, lowers fabric shrinkage at increased temperatures, and increases resistance to cold.

Carbon black is a widely used filler. This is a carbon whose crystalline structure has a spherical shape. The basic forms of carbon black are channel black, gas black, anthracene black, lampblack, furnace gas black, oil burner black, and thermatomic black.

Channel blacks are the ones most generally used as fillers. They have the smallest particle size among the various forms of carbon black. The average particle size of carbon black is 250 - 500 Å; the particle size of furnace gas black is slightly greater than that of channel black.

Carbon black is second only to natural rubber in the production of rubber.

Ground limestone of average density is usable, and asphalt limestone or dolomite is also usable if it contains 4 - 8% high-melting bitumen and no more than 2% clay-like additives, and has a compression strength of not less than 200 kg/cm^2 .

TABLE 14. PROPERTIES OF POLYETHYLENE

Property	Type of polyethylene	
	A (no catalyst)	B (catalyst)
Density in g/cm ³	0.92 - 0.93	0.935 - 0.95
Limit of stability in kg/cm ² :		
during tension	84 - 175	195 - 395
during shrinking	125 - 210	-
during flexing	120 - 170	-
Relative elongation in %	150 - 600	100 - 200
Modulus of elasticity in kg/cm ² during tension	980 - 2450	3500 - 7000
Shore hardness	45 - 55	63 - 74
Degree of crystallinity in %	40 - 65	65 - 85
Molecular weight	15,000 - 35,000	25,000 - 100,000
Softening point in °C	105 - 120	126 - 135
Coefficient of thermal conductivity in kcal/m · hrs · degrees	0.22 - 0.28	0.26
Coefficient of linear expansion	0.00018	0.0001
Specific heat capacity in kcal/g · degrees	0.50 - 0.55	0.55
Dielectric permeability at 60°C and 10 ⁶ hz	2.2 - 2.33	2.2 - 2.3
Dielectric loss tangent at 60°C:		
10 ³ hz	0.0002	-
10 ⁵ hz	0.0003	0.0001 - 0.0003
10 ⁸ hz	0.0005	-
Volume resistivity in ohm · cm	10 ¹⁷	10 ¹⁷
Breakdown voltage in kv/mm	45 - 60	45 - 60

Pulverized stone is sifted through a sieve with 900 holes/cm²; the residue on the sieve should not exceed 2%.

Dry limestone (moisture content no more than 1%) without nodules or impurities should be introduced into warmed bitumen. It must be protected from moisture during shipment.

CHEMICAL COMPOSITION OF LIMESTONE IN %

CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Residue not soluble in 10% HCl	hygroscopic moisture	Loss on calcination
52.55	1.02	1.93	0.6	0.75	1.49	no more than 0.29	41.37

Syzranskiy asphaltite. Unlike limestone, asphaltite is not subject to moistening during storage and transit, since it is a water-repellent limestone.

Talc is a mineral of white color, a hydrous magnesium silicate which is soft and greasy to the touch.

GRANULAR COMPOSITION OF LIMESTONE IN %

Size of fractions in mm	0.25 -	0.05 -	0.01 -	0.005 -	> 0.001
	0.05	0.01	0.005	0.001	
% content	32.93	31.26	13.68	20.66	2.07

A diabasic powder of dark-green color is obtained during rock-crushing and is a poor silicon. Deposits of it are found in the Caucasus, the Ukraine and Karelia.

Andesite flour is a finely ground, acid-resistant powder obtained by milling pre-crushed andesite acid-resistant stone. It is intended principally for the preparation of acid-resistant plasters, mortars and concretes.

In physical and chemical properties it meets the following specifications: residue when screened through a sieve with a No. 06K mesh (GOST 3584-53) not more than 25%; acid-resistance not below 95%; moisture content not more than 3%.

COMPOSITION OF SYZRANSKIY ASPHALTITE IN %

CaCO ₃	MgO	Al ₂ O ₃	Fe ₂ O ₃	Residue not soluble in 10% HCl	SiO ₂	Hygroscopic moisture	Loss on calcination
54.39	1.29	3.54	-	1.91	0.2	0.37	40.3

CHAPTER TWO

RUBBER-BITUMEN AND POLYMER-BITUMEN INSULATING MATERIALS

Every coating consists of a primer, a layer of enamel, and wrapping material. The purpose of the primer is to make the enamel adhere to the surface to be insulated. The enamel is the basic insulating layer, protecting the steel surface from corrosion. The wrapping layer enhances the protective properties of the enamel, principally by protecting it from deformations and various mechanical injuries.

Brizol Wrapping Material

Brizol is a waterproofing material, replacing Ruberoid, tar paper, pergamyn and hydrosol, used in the construction industry for anti-corrosion protection of buried metal pipelines, waterproofing foundations, general-purpose roofs, septic systems and special hydraulic engineering installations, and for installation of flexible roofs. Brizol can be used as both a heat insulator and an acoustic insulator.

The main properties of brizol are its satisfactory stability, low water-permeability, high water-repellency, and good dielectric and heat-insulating properties. Among the merits of brizol must be included, in addition, its reasonable cost and its ease of preparation.

Brizol is made from several constituents: bitumen, rubber particles, asbestos and plasticizers. Used in the production of brizol are: granulated rubber from old auto tire treads (TU MKHP No. SHU-96-56); types IV and V bitumen (GOST 9812-61); type 7 asbestos (GOST 7-51); ozocerite (GOST 780-54); green oil (GOST 2985-51); type P-20 polyisobutylene and polyethylene.

Brizol of several types is currently being produced for various construction and pipeline operation conditions. Brizol is classified into vulcanized

or unvulcanized depending on how it is prepared, and into polymer (BR-P) and nonpolymer (BR-S; BR-M; BR-T) depending on the initial raw material used. Nonpolymer brizols are in turn classified into ordinary (BR-S), sea-stable (BR-M) and thermo-stable (BR-T), according to the conditions under which they are intended to be applied.

The various kinds of brizol differ little in protective properties. They do differ in physical and mechanical properties. The basic properties of brizol are shown in Tables 15 and 16. Table 17 shows the physical and mechanical properties of brizols from different factories.

TABLE 15. PROPERTIES OF BRIZOL

Property	Brizol	
	Unvulcanized	Vulcanized*
Limit of tensile strength in kg/cm^2	7 - 17	Up to 45
% elongation:		
relative	Up to 100	" 250
residual	" 35	" 15
Resistance to bending	No crack from slight angles through 180°	
Softening point in $^\circ\text{C}$	Up to 140°	Not softened
Water absorption in 24 hours in %	0.2 - 0.5	Up to 1
Resistivity after 3 years in corrosive medium in $\text{ohm} \cdot \text{cm}$	$10^{11} - 10^{12}$	-
Drop-off in ohm resistance after 5 months in 5% solution NaCl, in %	12	-

*NIISHP data

For specialized uses, brizol can be prepared to specifications from inexpensive fabric (packing, sackcloth, gauze, fiberglas). The fabric comes in widths up to 1.5 m. Brizol intended for general-purpose waterproofing is about 1.5 mm thick; for roofing it is 3 - 4 mm thick. If necessary, the thickness of brizol can be varied within limits of from 0.5 to 5 mm.

TABLE 16. PHYSICAL AND MECHANICAL PROPERTIES OF VARIOUS TYPES OF BRIZOL

Kind of brizol	% Elongation		Tensile strength in kg/cm^2	% Water saturation for 30 days	Softening point in $^\circ\text{C}$	Impact stability in kg/cm^2		Resistivity in $\text{ohm} \cdot \text{cm}$
	Relative	Residual				-15°	-20°	
BR-M, sea-stable (winter)	100	40	8	2.71	110	60	20	10^{10}
BR-T, thermo-stable	30	6	13.2	2.67	160	-	-	10^{10}
BR-P, polymer	70	30	17	2	140	60	40	10^{10}

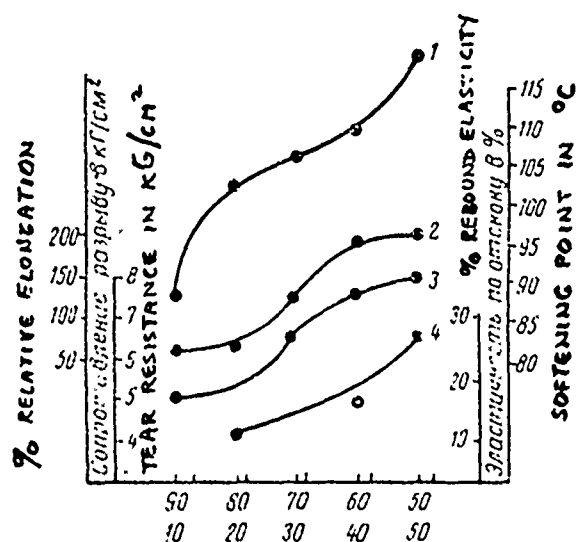
TABLE 17. PHYSICAL AND MECHANICAL PROPERTIES OF BRIZOL FROM VARIOUS FACTORIES

Property	Brizol rubber-recycling factories				Novokuybyshevskiy "Brizol" factory	
	Chekhovskiy	Sumskiy	Krasnoyarskiy	Bobruyskiy	BR-S	BR-P
Thickness in mm	1.6 ± 0.2	1.8 ± 0.2	1.6 ± 0.2	1.5 ± 0.2	1.4 ± 0.2	1.6 ± 0.1
Width in mm	425 ± 25	425 ± 25	500 ± 25	425 ± 25	425 ± 25	425 ± 25
Length in m	50 ± 1	50 ± 1	50 ± 1	50 ± 1	50 ± 1	50 ± 1
Tensile strength in kG/cm ²	6	7	8	7	9	17
% elongation relative	75	70	60	70	70	70
residual	35	30	35	35	35	15 - 35
% water absorption in 24 hours	0.5	1	1	1	0.5	0.5
No. of bends before appearance of cracks						
20 - 25°C	6	10	10	10	10	10
5°C	2	2	2	-	-	4 double bends at - 15°C

Depending on shipping and application conditions, brizol can be of any length. The weight of one square meter of brizol 1.5 mm thick is about 1.6 kilograms.

The constituents of brizol can be varied in accordance with techniques used, kinds of raw materials available, conditions of recycling, and types of equipment. Depending on composition, primarily the ratio of bitumen to rubber, the structural and mechanical properties of brizol vary. Specifically, when the rubber content in the brizol is increased, its tensile strength and relative elongation increase: when the rubber content is increased from 10 to 50% the tensile strength of the mixture is 1.7 times greater, and the relative elongation 4 times greater. It must be borne in mind that the change in these properties is of a discontinuous nature. When rubber content is increased, the elasticity of rubber-bitumen compositions is increased.

Adding plasticizers to brizol mixtures has made it possible to obtain a more elastic material of great mechanical stability, suitable for processing, and stable under service conditions. Such a plasticizer should at the same time act as an antiseptic for rubber-bitumen mixtures. Phenols meet these requirements; a phenol is a solution of polyisobutylene in green oil and shale, pine tar, and semi-coked resins. The optimal amount of plasticizer is 1% (large amounts decrease the stability of brizol) (Fig. 4). Depending on the type and amount of plasticizer, materials with good physical, mechanical and protective properties can be obtained (Tables 18 and 19).



Contents in percent of weight

Fig. 3. Dependence of physical and mechanical properties of brizol mixtures on their composition. 1 - softening point; 2 - relative elongation; 3 - tensile strength; 4 - rebound elasticity

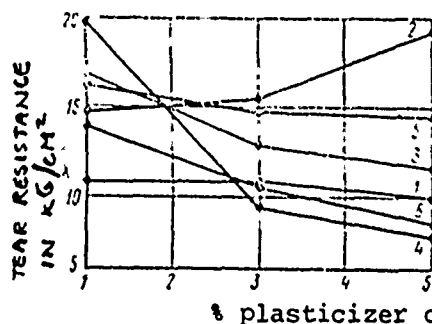


Fig. 4. Dependence of brizol stability on plasticizer content. 1 - axle grease; 2 - ozocerite; 3 - resin from rubber pyrolysis; 4 - polyisobutylene; 5 - pine tar resin; 6 - semi-coked resin.

TABLE 18. EFFECT OF PLASTICIZER ON PHYSICAL AND MECHANICAL PROPERTIES OF BRIZOL MIXTURES

Property	Plasticizer			
	Slaty resin	Pine tar resin	semi-coked resin	phenol
% elongation:				
relative	100	74	88	40
residual	33	30	31	18
Tensile strength in kg/cm^2	4.7	3.9	3.8	2.5

TABLE 19. EFFECT OF VARIOUS PLASTICIZERS ON WATER-SATURABILITY OF BRIZOL MIXTURES

Plasticizer	% water-saturability over	
	30 days	60 days
Dibutylphthalate	1.78	3.35
5% solution polyisobutylene, type P-200, in green oil	2.90	3.72
Ozocerite	2.90	3.79
Diethylene glycol dibutyrate	2.94	4.49
Ethylene glycol	5.57	7.63
Resins:		
pine tar	3.51	4.81
semi-coked	4.28	5.35
shale	5.14	8.60

Brizol of optimal composition (Table 20) is manufactured at the Chekhovskiy, Novokuybyshevskiy and Sumskiy factories. The physical and mechanical properties of these brizol compositions are shown in Table 21.

TABLE 20. % COMPOSITION OF RUBBER-BITUMEN COMPOSITIONS

Constituent	BR-P (Novokuybyshevskiy factory)	No. of composition (Chekhovskiy factory)				
		1	2	3	4	5
BN-IV	58	58	63	60	57	57
Granulated rubber	25	25	25	25	25	30
Asbestos	12	12	7	12	12	8
Ozocerite	-	5	5	3	4	5
Green oil	2	-	-	-	2	-
Polyethylene	3	-	-	-	-	-

TABLE 21. PHYSICAL AND MECHANICAL PROPERTIES OF RUBBER-BITUMEN COMPOSITIONS

Property	BR-P (Novokuybyshevskiy factory)	No. of composition (Chekhovskiy factory)				
		1	2	3	4	5
Tensile strength ₂ in kG/cm ²	17	7.9	7.2	7.5	7.0	7.2
Relative elongation in %	70	75	115	75	85	70
% Elasticity	20	14	14	14	14	15

Brizol waterproofing materials are used as a protective layer and may be employed under varying conditions. The composition and properties of brizol mixtures determine the applications and service conditions for which they are suitable. For example, the stability of brizol when exposed to light and heat

depends on the rubber content in the composition, and this stability in turn affects its usefulness under atmospheric conditions.

The stability of brizol in underground service also depends on the ratio of rubber to bitumen.

Table 22 gives data on the variation of physical and mechanical properties of brizol with rubber-bitumen ratio in one day of heat curing, and Table 23 shows the same for a ten-day period.

TABLE 22. VARIATION OF PROPERTIES OF RUBBER-BITUMEN COMPOSITIONS

Composition of mixture in %		Properties of composition					
		initial		after curing at 80°C			
bitumen (BN-IV)	rubber	tensile strength in kg/cm ²	relative elongation in %	tensile strength in kg/cm ²	% stability gain over initial	relative elongation in %	% decrease in elongation over initial
90	10	4.9	50	-	-	20	60
80	20	5.2	70	9	73	45	36
70	30	6.5	120	10	54	100	17
60	40	7.5	190	10.5	40	115	40
50	50	8	195	11.5	43	175	11

TABLE 23. VARIATION OF PROPERTIES OF RUBBER-BITUMEN COMPOSITIONS

Composition of mixture in %		Properties of composition					
		initial		after curing at 80°C			
bitumen (BN-IV)	rubber	tensile strength in kg/cm ²	relative elongation in %	tensile strength in kg/cm ²	% stability gain over initial	relative elongation in %	% decrease in elongation over initial
90	10	7.9	75	11.5	45	45	40
80	20	7.2	115	11.7	62	45	61
70	30	7.5	75	12.3	64	45	40
60	40	7	85	10.5	50	50	41
50	50	7.2	70	11	53	54	30

The increased stability and decreased elongation of rubber-bitumen mixtures during heat curing is caused by evaporation of the lightest fractions of bitumen --"drying." In such a process the bitumen becomes harder and even brittle.

Adding rubber to the bitumen affects its stability, since the rubber retains light oils and when it is incorporated into a bitumen composition it prevents "drying" of the mixture and retards the process of curing.

Figure 5 graphs the dependence of deformation of rubber-bitumen compositions on temperature, and Figure 6 shows dependence of brittleness temperature of a composition upon its rubber content.

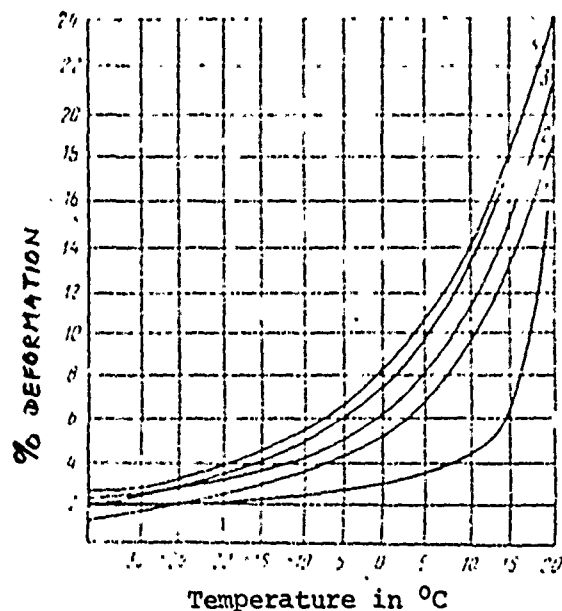


Fig. 5. Dependence of deformation of rubber-bitumen compositions on temperature (1 - 5 -- constituents as in Table 20)

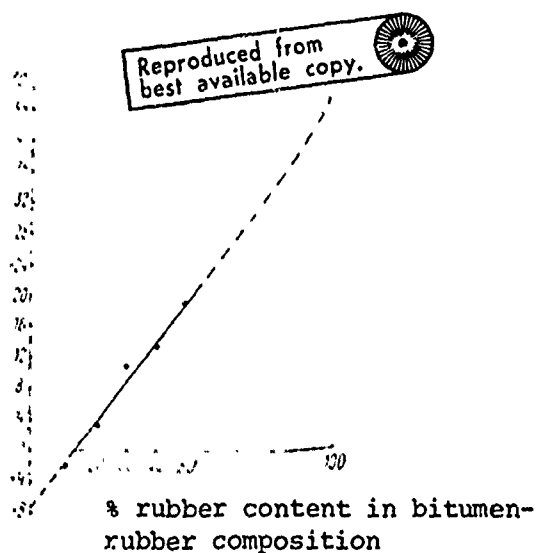


Fig. 6. Glass point and brittleness temperatures of rubber-bitumen composition (constituents are shown in Table 24)

Adding plasticizers (in an amount up to 5%) to the mixture sharply decreases the brittleness temperature of a rubber-bitumen mixture (Fig. 7). The maximum decreased brittleness temperature effect is observed when low-molecular-weight P-20 polyisobutylene or a 5% solution of P-200 polyisobutylene in green oil is added to the mixture.

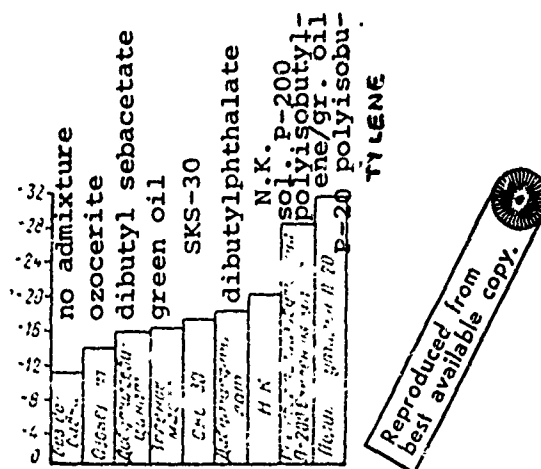


Fig. 7. Brittleness temperature of rubber-bitumen composition (70/30) in dependence on plasticizer

TABLE 24. VARIATION IN PROPERTIES OF RUBBER-BITUMEN COMPOSITIONS EXPOSED TO ULTRAVIOLET IRRADIATION

Composition of mixture in %		Duration of irradiation in hours											
		0		1		2		3		4		8	
		tensile strength	relative elongation in kG/cm ²	same	same	same	same	same	same	same	same	same	same
BN-IV	rubber												
90	10	4.9	50	-	-	-	-	-	-	-	-	6.2	+26
80	20	5.2	70	5	70	5.5	40	5.4	70	5.5	50	6.8	+31
70	30	6.5	120	5.5	100	5.2	115	5.1	100	6	120	6.5	0
60	40	7.5	190	6.3	140	6.5	100	6.2	120	-	-	6.8	-9
50	50	8	125	-	-	-	-	-	-	-	-	7.5	-6

Rubber-bitumen compositions with a 10 - 20% rubber content retain their stable properties during light curing. When rubber content is increased (up to 40 - 50%) the mixtures' properties deteriorate under light exposure (Table 24).

The waterproofing properties and durability of coatings under service conditions are determined by the decrease in the volume resistivity of an insulating coating with the passage of time.

Tables 25 and 26 give data on the variation of resistivity of bitumen compositions with the passage of time (coating thickness 3 mm).

The results of alternate freezing and thawing of brizol in a dry and a moist state are depicted graphically in Fig. 8. After 1.5-mm-thick brizol₂ had been in a salt medium for two years, its tensile strength was 10 kG/cm² (before testing 11.2 kG/cm²); correspondingly, relative elongation came to 123 and 130% and residual elongation to 14 and 20%, while the resistivity remained unchanged.

The physical and mechanical properties of brizol varied negligibly with repeated freezing (20 cycles).

TABLE 25. VARIATION OF VOLUME RESISTIVITY OF BITUMEN COMPOSITIONS, WET CONTACT METHOD, 5% NaCl SOLUTION

Make-up of Composition	Volume resistivity in ohm · cm			
	initial	after 3 months	after 6 months	after 9 months
Bitumen BN-IV + + 20% kaolin	$7.2 \cdot 10^{11}$	$6.75 \cdot 10^9$	$2.7 \cdot 10^6$	$2.2 \cdot 10^6$
Bitumen BN-IV + + 20% rubber	$4 \cdot 10^{11}$	$3.57 \cdot 10^{11}$	$3.60 \cdot 10^{11}$	$2.25 \cdot 10^{11}$

TABLE 26. VARIATION OF VOLUME RESISTIVITY OF BITUMEN COMPOSITIONS IN GROUND SATURATED WITH 5% NaCl SOLUTION

Make-up of Composition	Volume resistivity in ohm · cm in the ground					
	pebbles		sand		loam	
	initial	6 months	initial	6 months	initial	6 months
BN-IV bitumen + + 20% kaolin	$4 \cdot 10^{12}$	$4.9 \cdot 10^5$	$5.5 \cdot 10^{12}$	$4.5 \cdot 10^6$	$4.5 \cdot 10^{12}$	$1.3 \cdot 10^7$
BN-IV bitumen + + 20% rubber	$6.7 \cdot 10^{12}$	$1.8 \cdot 10^8$	$1.8 \cdot 10^{12}$	$1.3 \cdot 10^{12}$	$4.5 \cdot 10^{11}$	$1.3 \cdot 10^{11}$

Manufacturing technique for BR-P brizol. Figure 9 depicts a flow sheet for the manufacture of brizol by an automatic, continuous-flow method. This technique has been adopted in the Chekhovskiy, Sumskiy, Bobruyskiy and Novokuybyshevskiy factories. Brizol manufacture consists of the following operations. Bitumen, rubber particles, and finally plasticizer (or polyethylene)

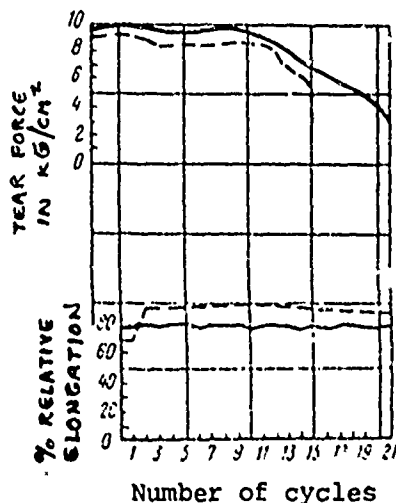


Fig. 8. Repeated freezing of brizol
— in dry state; ---- in moist state

are loaded into the mixer. No more than 5% polyethylene may be introduced into the brizol, since larger amounts harden the mass rapidly, which hinders its mixing. The mass is heated for from 1 hour, 25 minutes, to 1 hour, 30 minutes and constantly stirred at a temperature of 150 to 160°C (6 - 7 atmospheres pressure in the steam jacket). After the rubber swells and the

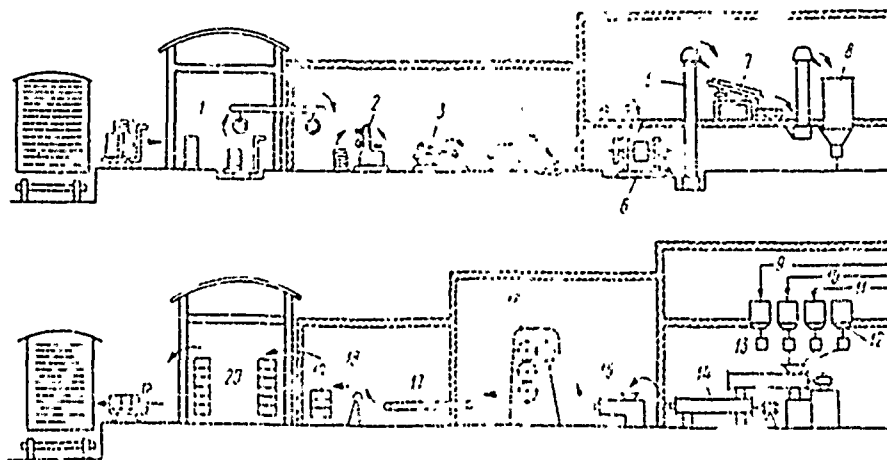


Fig. 9. Flow sheet for brizol manufacture by the automatic, continuous-flow method

1 - storage and weighing of old tire treads; 2 - sidewall trimming; 3 - mechanized shears; 4 - tire cutter; 5 - crushing rollers; 6 - elevator; 7 - vibratory sieve; 8 - storage bin for rubber particles; 9 - tank for pre-melting of bitumen; 10 - tank for melting of ozocerite; 11 - delivery bin for asbestos; 12 - delivery bin for granulated rubber; 13 - calibrated tank; 14 - continuously operating worm-conveyor blender for heating bitumen-rubber mixture; 15 - extruder; 16 - calender; 17 - shrinkage conveyor; 18 - take-up roller stand; 19 - intermediate storage of calendered rolls of brizol; 20 - storage of finished product

polyethylene melts, asbestos is fed into the mixer. The finished mass is discharged out of the mixer onto a board for dressing and then along a conveyor going away from the mixer; it is then fed into a rolling compartment, where it is worked for 20 - 25 minutes. Sheets are cut at intervals by mechanical jaws. The flattened mass is fed into calenders at a belt movement rate of 16 - 18 m/min; then the belt proceeds across a cooling roller, after which it is dusted with chalk and wound onto spools with a diameter of 65 - 70 mm in 55-m lengths, with an allowance for 10% shrinkage of the brizol fabric. During calendering of the soft, sticky mass of brizol, the speeds of rotation of the calender rollers must be different for normal passage of the fabric from the upper onto the middle and then onto the lower discharge roller. The following ratio of speeds of rotation of calender rollers is optimal:

upper roller	0.9
middle roller	1
lower roller	1.1

It is very important to cool the brizol fabric down to room temperature on a special conveyor handling the output of the fabric from the calender: as the hot fabric is spooled it is warped and sticks together (at +50°C brizol has a shrinkage of 25 - 30%).

A sufficiently long belt conveyor must be set up for normal cooling of the brizol fabric, or else augmented cooling must be used --passing the brizol

fabric across cooling drums or through a water bath, or air-cooling it.

If the brizol is run out on a tissue or other backing, it is covered with the rubber-bitumen mixture on the same calender, which should have an auxiliary device for flattening and truing the reinforcing material.

Vulcanizing agents are introduced into the brizol mixture to vulcanize it. This operation is performed in continuously operating drum vulcanizers or compartments, the same as for vulcanization of rubberized fabric. Brizol may also be vulcanized after it has been well dusted, following calendering in rolls in ordinary vulcanizing tanks (ambient air at 143°C).

Brizol is shipped to the construction site in rolls.

A permanent-paint mark is applied on each roll, after which it is tied with binder twine. The rolls must be stored in lots and transported under such conditions that the brizol is protected from rainfall and heating by the sun. Brizol is kept in closed sheds for long-term storage. Brizol rolls are covered with tarpaulins or roofing material during transport on motor vehicles and during short-term storage at the work site.

Brizol may be stored for a period of not more than four months. It must be stacked in piles horizontally, not more than four rolls high.

Technical and economic factors. Rubber items which are no longer of any use (automobile tire treads) are a source of raw materials for the production of rubber-bitumen insulation. Thus no additional agents are required for the manufacture of such a material.

At the present time more than 6000 km of main oil and gas pipelines alone are insulated annually. If it is considered that approximately 30% of all pipelines are insulated by brizol, then the annual economic cost, counting only main pipelines with a diameter of 720 mm, amounts to about 293,000 rubles.

The use of rubber-bitumen insulation instead of the mineral-bitumen kind previously in vogue has made it possible to extend the interval of time between repairs, curtail expenditures for overhauling and operational expenses, and decrease the standard rates of amortizing deductions.

Anti-Corrosion Enamels

Properties of enamels. Rubber-bitumen enamels (microstructure shown in Fig. 10) --the main insulating layer-- can be used at ambient temperatures from $+30$ to -30°C . They should be highly adhesive to metal and wrapping material.

The correct selection and assignment of insulating materials (considering their service life in the project) are inseparably related to the structural and mechanical properties of the material. For example, the material should either not be deformed at all by an organic binder under load, or a significant

portion of the deformation should be of a resilient nature, i.e. after the load is removed it should disappear (as, for example, in rubber). This can be accomplished by introducing rubbery materials into the composition of a bitumen binder, so that only resilient deformations will occur under load, and flow will not occur.



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Fig. 10. Microstructure of bitumen-rubber system

TABLE 27. EFFECT OF VARIOUS AMOUNTS OF PULVERIZED RUBBER ON PHYSICAL AND MECHANICAL PROPERTIES OF ENAMEL

Enamel composition in %		ring and ball softening point °C	extensi- bility in cm	depth of needle pene- tration in 0.1 mm at +25°C	brittleness temperature in °C
bitumen	rubber				
100	0	71	4	18	+5
99	1	73	4.7	17	0
95	5	82	3.1	15	-5
90	10	98	3	15	-10
85	15	106	2.5	11	-10

In molten bitumen the rubber is partially devulcanized, partially dissolved, forming a capillary network of devulcanized rubber which reinforces the material imparting elastic and plastic properties to it.

The percentage of rubber added can be varied, according to the properties of the enamels required. Table 27 gives data on the effect of the amount of pulverized rubber on the physical and mechanical properties of enamel.

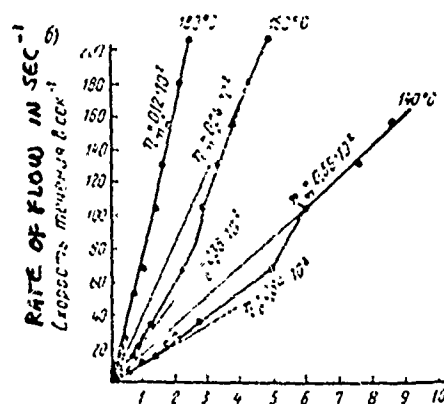
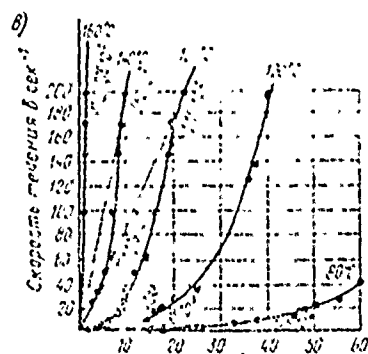
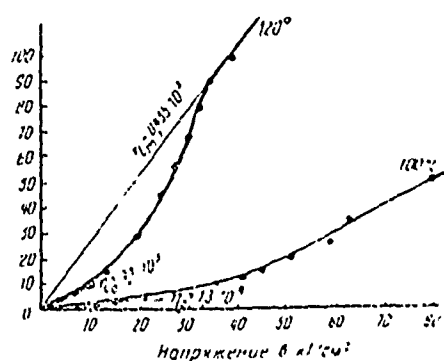


Fig. 11. Rheograms at various temperatures. Top two graphs - rubber-bitumen enamel; other - BN-IV bitumen (η_0 - maximum viscosity; η_m - least plastic viscosity) Horizontal - stress in kg/cm^2 ; vertical - rate of flow in sec^{-1}

The increased viscosity of the rubber-bitumen enamel makes it possible to apply it by a mechanically propelled device to a given thickness (4 - 6 mm) Pipelines insulated with rubber-bitumen enamel which is plasticized by green oil can be laid in a trench at an ambient temperature as low as -30°C without rupture of the insulating coating.

When rubber is introduced, the softening point of the rubber-bitumen enamel increases in steps, the enamel is considerably stiffened, and its viscosity and elasticity are markedly increased.

Fig. 11 shows flow curves of bitumen and rubber-bitumen enamel at various temperatures, and Table 28 shows rheological characteristics of the enamel and of the bitumen (for comparison).

Rubber-bitumen enamel has significant advantages over presently used mineral-bitumen enamel. For example, adding rubber up to 7% increases the softening point by $1.5 - 2^\circ\text{C}$, and 7 - 12% increases it by $3 - 4^\circ\text{C}$. When up to 30% mineral filler (kaolin) is added, each percent of it raises the softening point by 0.3°C , and between 30 - 50%, by 1°C (Fig. 12). At 80°C the viscosity of a rubber-bitumen enamel containing 5% pulverized rubber equals the viscosity of enamel containing 35% mineral filler; one containing

TABLE 28. RHEOLOGICAL CHARACTERISTICS OF RUBBER-BITUMEN ENAMEL AND BITUMEN

Sample	t, °C	η_0 (limiting viscosity), poise	η_m (Least plastic viscosity), poise
BN-IV bitumen	100	$7 \cdot 10^3$	-
	120	$1 \cdot 10^3$	$1.15 \cdot 10^2$
	140	$1.3 \cdot 10^2$	$0.52 \cdot 10^2$
	160	-	$0.76 \cdot 10^1$
Rubber-bitumen enamel (93 parts by weight BN-IV, 7 parts by weight rubber)	100	$1.3 \cdot 10^4$	-
	120	$6.1 \cdot 10^3$	$0.435 \cdot 10^3$
	140	$2.89 \cdot 10^2$	$0.56 \cdot 10^2$
	160	$0.38 \cdot 10^2$	$0.24 \cdot 10^2$
	180	-	$0.12 \cdot 10^2$

12% rubber equals the viscosity of an enamel containing 45% mineral filler. This shows that as temperatures increase, the difference in viscosity properties between rubber-bitumen enamel and mineral-bitumen enamel is especially noticeable.

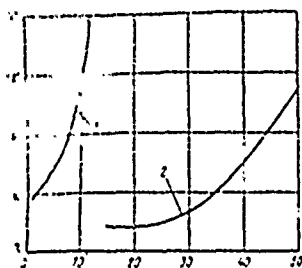


Fig. 12. Dependence of softening point of bitumen enamel on type and amount of filler. 1 - rubber; 2 - kaolin

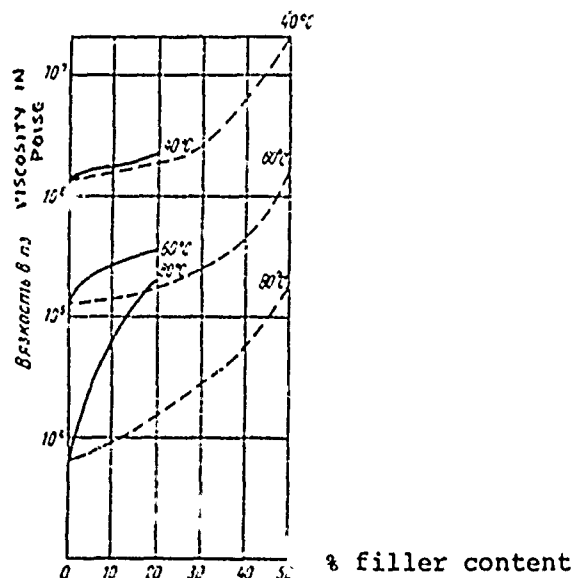


Fig. 13. Dependence of viscosity of enamels on temperature. — rubber-bitumen enamel; ---- mineral-bitumen enamel

From Fig. 13 it follows that at increased temperatures the pulverized rubber acts not only as a filler, but also as a plasticizer. This is shown by the sharp increase of viscosity curves with increased rubber content.

The lower nominal yield point P_k (resilient properties) for rubber-bitumen enamel with a 1% rubber content coincides with the same for a mineral-bitumen enamel only at a mineral filler content of 30%. The sloping nature of the curves of mineral-bitumen compositions demonstrates the negligible increase in resilience of the enamel when the quantity of filler is increased.

The upper nominal yield point P_k of the enamels (plastic properties) at various filler contents is shown in Fig. 14.

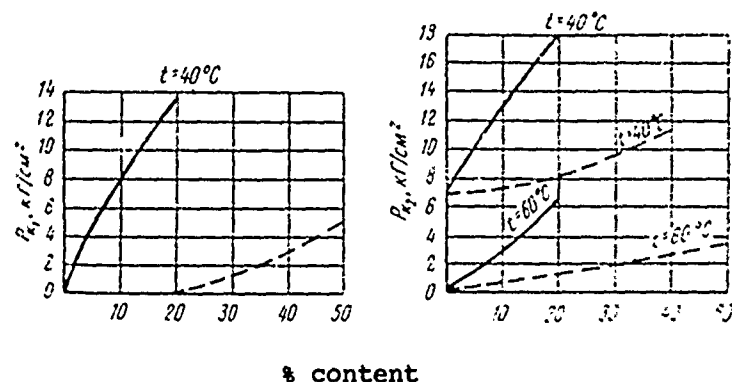


Fig. 14. Dependence of nominal yield point of enamels on quantity of filler (same notation as in Fig. 13)

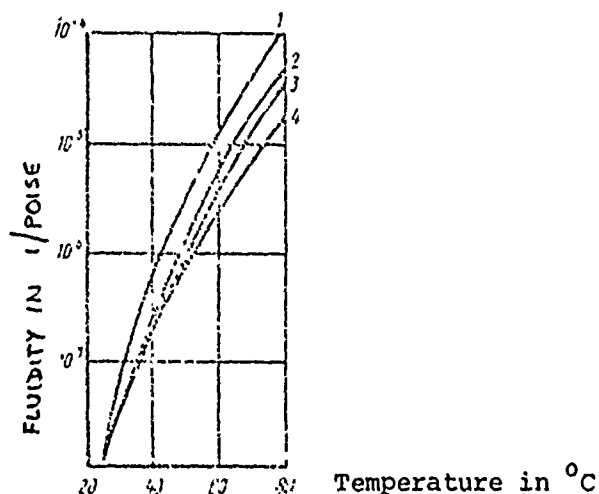


Fig. 15. Dependence of fluidity of bitumen and enamel on temperature
1 - bitumen; 2 - mineral-bitumen enamel (5% kaolin); 3 - same with
25% kaolin; 4 - rubber-bitumen enamel (7% rubber)

Another advantage of rubber-bitumen enamel over mineral-bitumen enamel is its lower flow rate (Fig. 15).

The properties of rubber-bitumen enamels can be improved if plasticizers are included in their composition.

The effect of petroleum and polymer plasticizers on the physical and mechanical properties of rubber-bitumen enamel (7% content of pulverized rubber) depend on variation of adhesion and plasticity, and also of refractoriness and elasticity at various temperature. To impart plasticity to refractory enamels with a softening point of 80 - 90°C, 5 and 7% plasticizer is added to them (Tables 29 and 30).

From a comparison of curves 1 and 2 (Fig. 16) it follows that below 0°C results for enamels with 5 and 7% plasticizer are close. Their adhesion stability averages 4.4 - 4.9 kg/cm² at -10°C and 2.8 - 3.5 kg/cm² at -20°C.

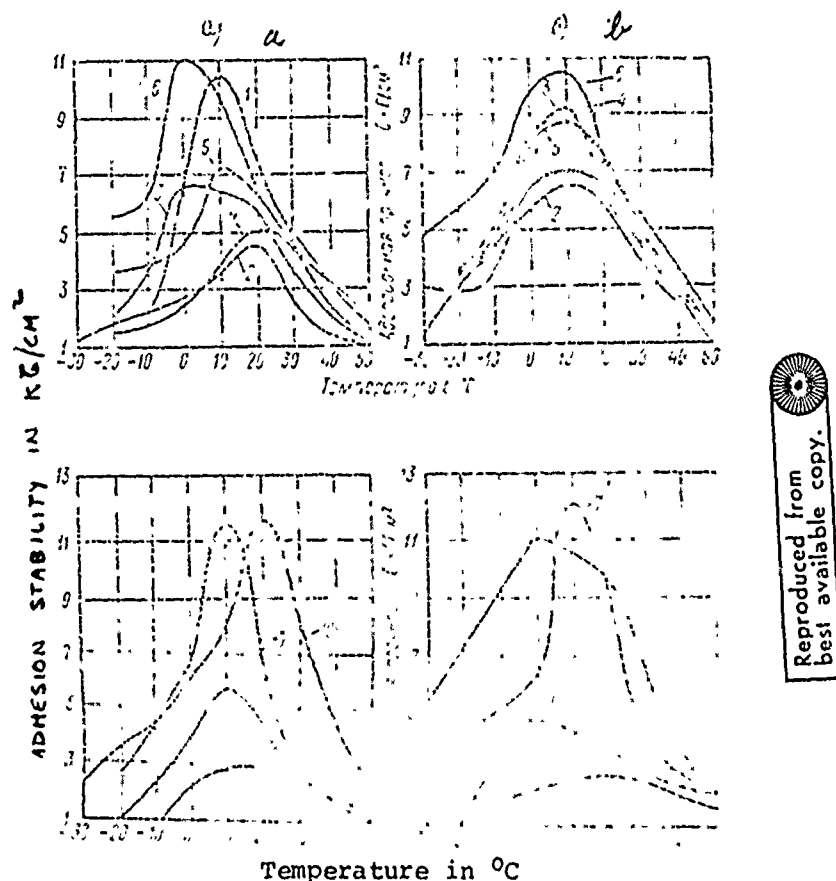


Fig. 16. Adhesion stability of plasticized enamels
 a - 5% plasticizer; b - 7% plasticizer; petroleum
 oils: 1 - spindle; 2 - transformer; 3 - distillate
 from recycled oil; 4 - automotive AKZ-10; 5 - axle
 grease; 6 - green oil; polymers: 7 - 5% solution of
 P-200 polyisobutylene in green oil; 8 - P-20 poly-
 isobutylene; 9 - low-density polyethylene; 10 - poly-
 diene

The exception to this would be enamels plasticized by green oil; their adhesion stability at -10 and -20°C is, respectively, 5.6 and 6.4 kg/cm^2 (maximum value 11 kg/cm^2 at 0° and $+10^{\circ}\text{C}$). When the temperature is increased up to 50°C the structural stability drops to $1 - 2 \text{ kg/cm}^2$.


Refractoriness of rubber-bitumen enamels containing plasticizers is ascertained by the decrease in viscosity and softening point. Petroleum plasticizers, as well as polydiene and a solution of polyisobutylene in green oil, lower the softening point of a rubber-bitumen enamel an average of $11 - 15\%$ below the initial value, i.e. down to $80 - 84^{\circ}\text{C}$.

This also lowers the least plastic viscosity: from $7.2 \cdot 10^4$ poise for the initial rubber-bitumen material to $4.7 \cdot 10^4$ for enamel with automotive oil and polydiene, and to $2.47 \cdot 10^4$ poise for enamel with spindle oil.

Low-molecular-weight P-20 polyisobutylene and polyethylene increase the softening point of an enamel with 5% polyisobutylene P-20 $\eta = 1.2 \cdot 10^5$ poise at 80°C . Polymer products are acknowledged to be the best plasticizers: polyisobutylene of varying molecular weights, and polydiene.

TABLE 29. PHYSICAL AND MECHANICAL PROPERTIES OF PLASTICIZED RUBBER-BITUMEN ENAMELS

plasticizer	Ring and ball softening pt °C	Elonga-tion in cm	5% plasticizer plasticity (penetration) at tem-peratures in °C in 0.1 mm										7% plasticizer plasticity (penetration) at tem-peratures in °C in 0.1 mm									
			-30	-20	-10	0	+10	+20	+25	+30	same	-30	-20	-10	0	+10	+20	+25	+30			
Enamel with-out plasti-cizer	101	1.1	2	3	4	5	6	9	10,5	12,5												
Petroleum plastici-zers: AU spindle oil	92	3	4	5	7	9	10,5	14	18,5	23												
transfor-mer oil	89	3	4	5	6	8	10,5	14	17	20,5												
transfor-mer (recy-cled) dis-tillate	88	3.4	3,5	4,5	6,5	—	12,5	18	19	25,5												
PKZp-10 automotive oil	88.5	3.1	4	5	6	8	10	14,5	16	20												
axle grease	91	3	4	5	6	8	10	14,5	16	20												
green oil	93	4	5	6	8	11	14	18	22,5	31												
Polymer plasticizers: 5% P-200 polyisobuty-lene in green oil	85	3.6	4	5	6	9	11	14	16,5	22												
low-molecu-lar P-20 polyisobuty-lene	120	0.6	2,5	3,5	4,5	5	7,5	10	13	15												
low-molecu-lar poly-ethylene	107	1.2	2,5	3,5	4,5	5	6	8,5	11,5	12,5												
polydiene	90	2.6	3	3,5	5	6,5	8,5	12,5	14	18												




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TABLE 30. ADHESION TO STEEL OF PLASTICIZED RUBBER-BITUMEN ENAMELS

Plasticizer	Adhesion stability (in kg/cm ²) of enamel															
	7% plasticizer															
	at a temperature in °C															
	-70	-60	-50	-40	-30	-20	-10	0	+10	+20	+30	+40	+50	+60	+70	+80
Enamel without plasticizer	—	1,5	3,4	4,4	4,7	4		4,5	2,1	—	—	—	—	—	—	—
Petroleum plasticizers:																
AU spindle oil	—	—	2,1	6,5	10,2	7,3		5	1,8	—	3,7	3,3	6,6	7,1	7	4,8
Transformer oil	1,3	2	2,3	2,6	2,7	4,5		2,8	1,1	3,1	2,8	4,7	5,7	6,6	5,9	3,7
Transformer (recycled) distillate	0	2,2	3,6	6,4	6	5,7		3,5	1,2	0	2,5	4,8	8,2	9,1	7,1	4,4
PKZp-10 automotive oil	0	1,6	—	2,8	3,9	5,1		4,5	1,3	1,6	2,9	4,9	8,1	9,3	6	4,6
Axle grease	—	—	—	—	—	—		4,6	2	—	3,5	4,2	8,2	8,8	7,6	4,9
Green oil	—	—	—	1,1	3,3	6,5		—	—	4,9	6	6,4	9,7	10,5	7,1	6
Polymer plasticizers:																
5% P-200 polyisobutylene in green oil	0	2,2	4,5	6,5	11,6	7,1		3	1,2	0	4,3	5,5	5,9	12,3	9,3	4,2
Low-molecular P-20 polyisobutylene	0	1	2,1	2,2	3,6	4,5		2,5	2	0	1,1	3,5	4,8	2,5	3,7	2,9
Low-molecular polyethylene	0	0	6,6	10,5	12,8	7		2,5	1,5	0	0	1,9	2,3	2,6	2,8	2,6
Polydiene	2,5	7	1,3	—	7,7	11,8		6,4	2,5	5,6	7,6	5,4	11,1	10,8	3	6,4



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Plasticizing bitumen enamels with polymers keeps their viscosity stable as the temperature is increased. The thermal stability of such enamels, unlike that of enamels plasticized by petroleum oils, is not substantially decreased. One polymer or another is selected, depending on the enamel properties desired: for example, polyethylene increases refractoriness, but below 0°C it lowers adherence qualities. Polydiene and a 5% solution of polyisobutylene P-200 in green oil have the opposite effect (at -30°C the adherence of enamel with polydiene is 2.5 - 5.6 kg/cm²).

Bitumen enamels containing 7% of various petroleum plasticizers can be painted onto structures (pipelines) at temperatures down to -30°C.

Manufacturing techniques. Enamel is presently manufactured under both factory and field conditions. The process of preparing the enamel under field conditions is very complicated and laborious, inevitably involving departures from standard techniques and, consequently, lowered quality of the coating.

Under field conditions, due to irregular and abrupt heating and intense oxidation, the bitumen mass obtained is non-homogeneous and more brittle than it should be. Thus the protective properties of an enamel prepared under these conditions and based on hardened bitumen are somewhat decreased, especially at their limits (which cannot be tolerated).

To improve the quality of insulating coatings and decrease the laboriousness of insulating techniques, the enamels must be prepared in bitumen-supply factories. Only in a factory can formulations for compositions be accurately followed, and the correct techniques used to ensure good enamel quality.

Bitumen enamel is presently produced by the Syranskiy insulating materials factory, the Gor'kovskiy (26 Bakinskiy Commissars) petroleum oil factory, and the Novo-Gor'kovskiy petroleum recycling plant. The most up-to-date techniques are employed in the Gor'kovskiy and Novo-Gor'kovskiy factories. They use an effective method for mixing the mass with live steam (temperature 270°C). This factory prepares enamel from bitumen which is fed into a mixer from a bitumen supply line coming directly from an oxidizing vat at the petroleum recycling plant; the bitumen is at 270°C. Then pulverized rubber is fed into the mixer and mixed with bitumen at 210 - 240°C by means of dry steam with a temperature of 250 - 270°C. The heat needed to maintain the cooking process is supplied uniformly through the whole volume of the mass, which obviates hot spots and overheating of the bitumen. A steam phase, forming over the surface of the mass and containing products of vaporization of bitumen and steam (lightest bitumen fractions, H₂O, CO₂), curtails the admission of oxygen and lowers the intensity of bitumen oxidation. This makes it possible to maintain the higher heating temperature (210 - 240°C) which is needed for more complete devulcanization of the rubber; as a result, the enamel's viscosity, softening point, and frost-resistance are increased.

To meet the requirements of construction and pipeline operation, formulations and manufacturing techniques (MRTU-12N-125-64) have been developed for the manufacture of three types of rubber-bitumen enamel --thermally stable

ones with a ring and ball softening point of 90 or 100°C (types MBR-IL-90 and MBR-I-LT-100), and a winter rubber-bitumen enamel with a softening point of 80°C (MBR-IZ-80).

Fig. 17 shows a flow sheet for manufacturing enamels at the Gor'kovskiy petroleum oil factory.

Manufacturing enamels by means of steam mixing of the mixture has the following advantage: the boiling point of the enamels is raised, so that devulcanization of the rubber is more thorough (Fig. 18).

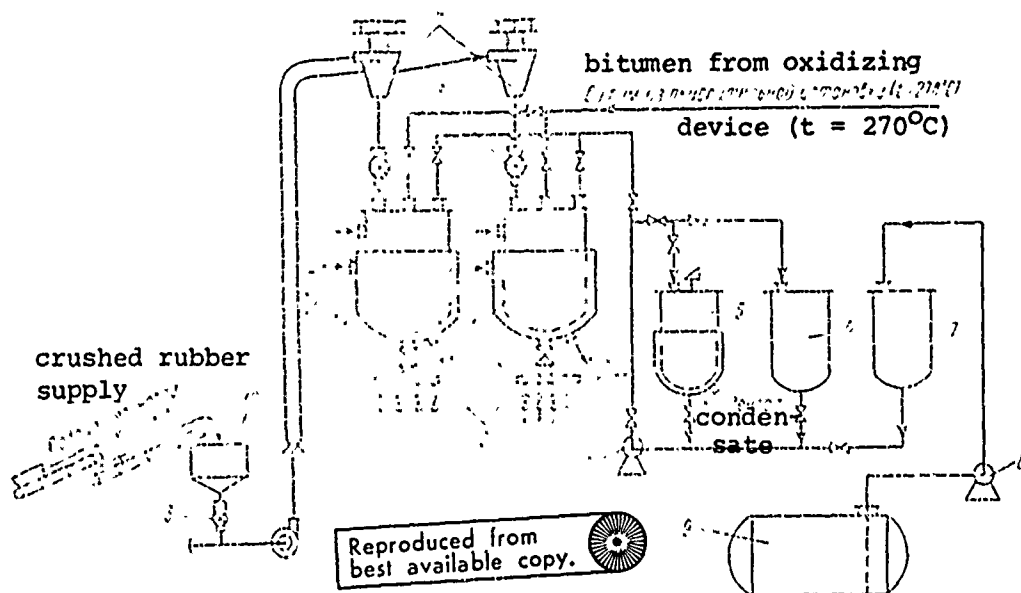


Fig. 17. Flow sheet for manufacturing enamel

- 1 - mixer with steam jacket; 2 - pouring device; 3 - sluice valves;
- 4 - cyclones; 5 - switch for mechanical mixing to prepare plasticizer;
- 6, 7 - plasticizer vessels; 8 - deposition; 9 - green oil storage vessel; 10 - pulverized rubber bin

A comparison of the properties of rubber-bitumen enamels obtained by steam and mechanical means of mixing indicates that the steam means produces enamels with the best structural and mechanical properties. For example, the viscosity of a rubber-bitumen enamel steam mixed at 20°C is $\eta_m = 5.3 \cdot 10^{10}$ poise and the nominal resilience limit $P_{k1} = 16.3 \text{ kg/cm}^2$, whereas for enamels mixed mechanically with open flame heating (field method of preparing enamel) $\eta_m = 1.8 \cdot 10^{10}$ poise and $P_{k1} = 14.1 \text{ kg/cm}^2$. The effective viscosity at a stress of $P = 23 \text{ kg/cm}^2$ is $2 \cdot 10^{11}$ poise for steam-mixed enamel and $2.3 \cdot 10^{10}$ poise for mechanically mixed enamel.

The elastic and viscous properties of enamels prepared by different methods vary even more widely in the range from 40 - 80°C. Fig. 19 graphs dependences of the nominal yield point and plastic viscosity of enamels upon temperature. From Fig. 19 it follows that the nominal yield point of a steam-mixed enamel is greater than that of an enamel which is mechanically

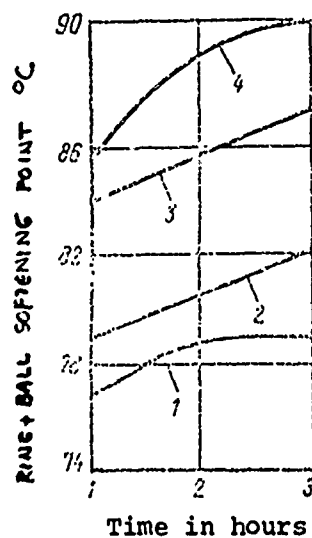


Fig. 18. Dependence of softening point of rubber-bitumen enamel on time and temperature of boiling

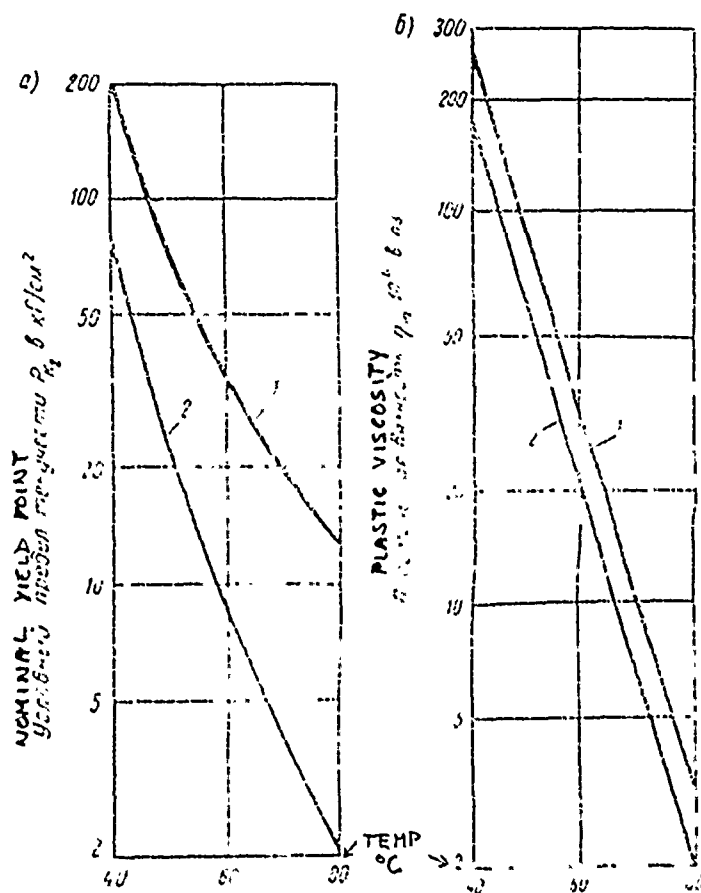


Fig. 19. Dependence of yield point (left) and plastic viscosity (right) of rubber-bitumen enamel on temperature, with different means of mixing. 1 - steam mixing; 2 - mechanical mixing.

mixed. This difference increases as temperature increases. Thus at 80°C P_{k2} is almost an order of magnitude greater for a steam-mixed than for a mechanically mixed enamel.

The plastic viscosity η_m of enamels falls uniformly with increase of temperature in the range from 40 - 80°C (Fig. 19 b). The nature of the temperature dependence of η_m is identical for these enamels; however, viscosity η_m is one and a half times greater for the steam-mixed enamel than for the mechanically mixed enamel, with open flame heating. Fig. 20 shows the dependence of the effective viscosity of enamels on shear stress at 40°C.

However, since existing factories are not able to meet the increasing needs of the construction industry for enamel, the enamel is also prepared under field conditions.

Open bitumen-melting pots of several types are used for field preparation of enamels. The best of these is the BK-81 type, in which the mixture is mixed mechanically. The preparation temperature for the enamel should not exceed 160 - 180°C. A higher temperature (up to 200°C) is allowable for a duration of no more than one hour. Increasing the temperature above 200°C can cause coking and ignition of the enamel (flash point does not exceed 230°C).

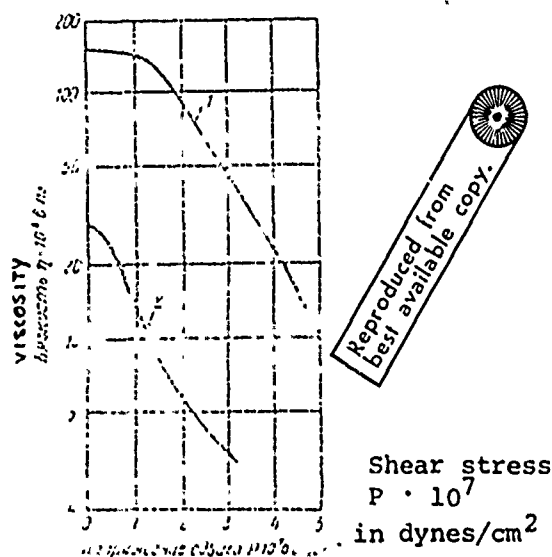


Fig. 20. Dependence of effective viscosity of differently prepared rubber-bitumen enamels on stress (notations as in Fig. 19)

The bitumen pot is heated via its exterior walls by an open flame, or, less commonly, by electrical means.

Enamel is prepared in the following manner. Bagged bitumen entering the production line from the petroleum recycling factory is crushed into chunks of about 5 kg in weight and loaded into tanks, where it is melted, dried, and mixed with a filler --pulverized rubber (added in amounts of from 3 to 12%, depending on the purpose of the enamel).

If no BN-IV bitumen is available, it can be prepared by mixing BN-III and BN-V bitumen (30 - 40% BN-III is usually used). In this case, the BN-III bitumen is loaded into the tank first. During drying the BN-III bitumen froths. When frothing is over, BN-V bitumen is loaded into the tank. The mixture froths again. The filler is put into the tank, and the bitumen is then completely dried.

Preliminary loading of slightly oxidized type BN-III bitumen, which is usually more moist than highly oxidized BN-V bitumen, ensures a higher-grade enamel: prolonged cooking of BN-III only slightly aids the process of its oxidation, whereas prolonged boiling of BN-V bitumen degrades its quality, lessens its oil and resin content, and thus makes it even more brittle.

Polydiene-Bitumen Enamel (Bitudiene)

The outstanding feature of this enamel is the fact that all types of bitumens (including low-plastic) can be used to prepare it.

During the preparation of bitudiene various specially prepared rubbers serve as admixtures.

Good results are obtained by using intermediate products of the manufacture of divinyl rubber --polydiene and coagulum.

Polymer-bitumen compositions with different properties can be obtained by varying the qualitative composition of the polymers used and the method of mixing them with the bitumen. Obtaining polymer-bitumen materials depends to a significant degree on bonding effects between the kind of bitumen used and the other constituents. For example, peroxidized bitumen is almost a polymer in molecular weight, which facilitates better bonding of the constituents of the polymer-bitumen.

Peroxided bitumen has an unusual physical and chemical make-up, in that it has a considerable content of resinous components with high molecular weight.

As the softening point of peroxidized bitumen is raised, its resin content increases, which enhances the elastic and plastic properties of bituminous compositions.

The process of combining bitumen with polydiene does not require a great deal of time; the process of preparing the enamel can therefore be continuous.

The structural and mechanical properties of the composition obtained depend on the degree of oxidation of the bitumen and the amount of polydiene introduced: with a softening point of 124°C the elongation is 1 cm and needle penetration depth is 8; with a softening point of 80°C the elongation is 4 cm and the needle penetration is 22, and so on.

The following basic properties are characteristic of bitudiene: homogeneity, thermal stability and resistance to cold (compositions with a softening

point of 70°C, elongation of 4 cm and needle penetration depth of 33, when painted 3 mm thick on pipelines and then reinforced by fiberglass, sustained ten freeze-thaw cycles), high dielectric properties, well-adjusted viscosity -- the viscosity of thermally stable enamel is $7.3 \cdot 10^5$ and that of plastic enamels is $8 \cdot 10^5$; i.e. they are almost equivalent. The greatest difference (almost an order of magnitude) is seen at 80°C. The brittleness temperature of refractory polydiene-bitumen compositions is 5°C; that of more plastic ones is 20°C.

Thermally stable and plastic polydiene-bitumen compositions have resilience and plastic properties: under a shear stress of P_{k2} the yield point of plastic compositions is exceeded by thermally stable compositions: at 40°C the yield points are 12 and 9 kg/cm², respectively; at 60°C 8 and 6.6 kg/cm²; and at 80°C 1.4 and 0.2 kg/cm².

At a temperature from 0 to 15°C the deformation of the system under a stress of 1.6 kg/cm² is equal to 2.5 - 4.5%; deformation is halved going from above to below 0°C. The regularity is maintained, in that when the load is increased to 5 kg/cm² deformation amounts to 5% at 0 - -15°C and 10% at 0 - -10°C.

TABLE 31. COMPARATIVE CHARACTERISTICS OF VARIOUS BITUMEN ENAMELS

Enamel	tg σ	ρ , ohm · cm	ϵ
Polydiene-bitumen	0.052	$1.7 \cdot 10^{11}$	6.41
Rubber-bitumen	0.04	$1 \cdot 10^{14}$	7.12
Mineral-bitumen with copper naphthenate added	0.06	$1 \cdot 10^9$	9.12

Table 31 gives data on the protective properties of polydiene-bitumen compositions; data on other materials are shown for comparison.

The protective properties of polydiene-bitumen coatings kept in a corrosive medium under superimposed current are stable; under extreme operational conditions (superimposed voltage of 25 v) the current shows an effect on the 3-mm-thick coating only after 5 years.

An enamel obtained from low-plastic bitumens from recycled petroleum has been successfully applied to a portion of the Iuzhgazoprovodstroy (note: Southern Gas Supply Line) and has exhibited good protective qualities over some years of service.

Specifications are available for the manufacture of two types of polydiene-bitumen enamel --winter and summer (Table 32).

Polydiene-bitumen enamel is produced under factory and field conditions from type IV and V bitumens mixed in varying proportions. Techniques are similar to those used for rubber-bitumen enamel.

TABLE 32. PHYSICAL AND MECHANICAL PROPERTIES OF POLYDIENE-BITUMEN ENAMELS

Property	Type of enamel	
	winter	summer
Ball and ring softening temperature °C	70	90
Needle penetration depth at 25°C in 0.1 mm, not less than	30	20
Elongation at 25°C in cm, not less than	4	3

Polyethylene-Bitumen Enamel (Bitulene)

The most notable thing about bitulene is the fact that sub-standard and unstabilized, low-density, powdered polyethylene can be used in preparing this refractory insulating material.

The physical and mechanical properties of bitulene at various polyethylene contents are shown in Tables 33 and 34.

TABLE 33. PHYSICAL AND MECHANICAL PROPERTIES OF BITULENE

Polyethylene content, %	B&R softening point °C	Elongation in cm	Needle penetration in 0.1 mm, at °C					Tear resistance (pull in kG/cm ²)	% water saturability over number of days			
			25	0	-5	-10	-20		1	3	10	30
0	72.5	3.6	16	3	2	1	0	5.6	0.1	0.17	0.3	0.6
1	81	3	11	2	1	0.5	0	5.2	0.045	0.11	0.24	0.54
2	85	2.2	12	2	1	0.5	0	5.5	0.043	0.11	0.29	0.57
3	86.5	1.7	12	2	1	0.5	0	5.7	0.073	0.2	0.38	0.71
4	98.5	0.8	8	1	0.5	0.5	0	5.5	0.05	0.15	0.35	0.61
5	100	0.6	8	1.5	0.5	0	0	4.9	0.06	0.17	0.37	0.62

TABLE 34. RHEOLOGICAL PROPERTIES OF BITULENE

Polyethylene content, %	Least plastic viscosity in poise			Nominal yield point P_{k_2} in kg/cm^2			Impact resistance in $\text{kg} \cdot \text{cm/cm}^2$ at coating thickness in mm					
							3			6		
	At a temperature in $^{\circ}\text{C}$											
	+40	+60	+80	+40	+60	+80	+20	0	-10	+20	0	-10
0	$1.5 \cdot 10^5$	$1.5 \cdot 10^5$	$6.8 \cdot 10^3$	10.5	0.67	0.06	15	10	8	15	10	10
1	-	-	-	-	-	-	14	6	4	17	8	7
2	$1.19 \cdot 10^5$	$4.6 \cdot 10^5$	$1.83 \cdot 10^4$	17.6	0.84	0.18	15	6	4	20	7	4
3	$4.1 \cdot 10^6$	-	$2.58 \cdot 10^4$	14	-	0.29	15	9	6	15	12	10
4	$5.16 \cdot 10^6$	$6.34 \cdot 10^5$	$5.06 \cdot 10^4$	13.5	1.73	0.24	15	7	6	18	8	6

Polyethylene-bitumen enamel is prepared by heat and mechanical means, under both field and factory conditions, from bitumen from the Syzranskiy factory which is obtained from Stavropol (note: "stavropol'skiy") petroleum

(which contains 1.65% sulfur and 4.5% paraffin hydrocarbons).

Tables 35 and 36 show the properties of polyethylene-bitumen compositions based on type IV bitumen from the Syzranskiy factory.

TABLE 35. PHYSICAL AND MECHANICAL PROPERTIES OF BITULENE

Property	No. of batch of enamel				
	1	2	3	4	5
R&B softening temperature, °C	95	95	98	90	89
Needle penetration in 0.1 mm at 25°C and stress of 100 G/5 sec	18	16	16	16	18
Elongation 5 cm/min in cm	2.8	2.6	2.8	3.2	3.4

The adhesion of polyethylene-bitumen enamels to the surface of a steel pipe is 5 - 6 kG/cm². This can be increased if the enamel is painted on at a temperature of 200°C.

TABLE 36. RHEOLOGICAL PROPERTIES OF BITULENE

No. of batch of enamel	Least plastic viscosity η_m in poise			Yield point P_{k_2} in kg/cm^2		
	At a temperature in $^{\circ}\text{C}$					
	40	60	80	40	60	80
2	$7.4 \cdot 10^6$	$8.8 \cdot 10^5$	$2.13 \cdot 10^5$	14.25	3.9	0.425
3	$5.2 \cdot 10^6$	$5.4 \cdot 10^5$	$1 \cdot 10^5$	13	3.1	0.425
4	$6.1 \cdot 10^6$	$7.8 \cdot 10^5$	$1.5 \cdot 10^5$	14.25	3.2	0.400

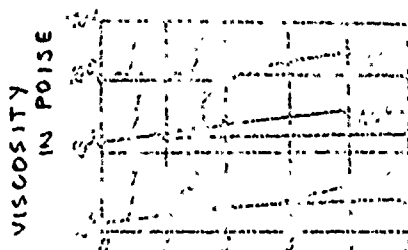


Fig. 21. Dependence of filler content on η_m at different temperatures. 1 - polyethylene; 2 - resin.

Compared with rubber-bitumen enamel, polyethylene-bitumen enamel has slightly greater viscosity (Fig. 21), greater stability in an alkaline medium, and less deformation. For example, at -15°C and various stresses, the deformation on compression of polyethylene-bitumen enamel is 1 - 2%, and at +15°C it is 6% for a stress of 5 kG/cm² and 12% for a stress of 8.5 kG/cm²; at -15°C a rubber-bitumen composition from Syzranskiy factory bitumen has a deformation on compression of 1.2 - 2%, and at +15°C it is 4 and 8% at stresses of 5 and 8.5 kG/cm², respectively.

Polyethylene-bitumen enamel is significantly less soluble in aromatic hydrocarbons than rubber-bitumen enamel: the amount of substance soluble in acetone is 8% for polyethylene-bitumen enamel and 26% for rubber-bitumen enamel.

The properties of polyethylene-bitumen enamel govern the realm of its applicability --protection of pipelines in oilfields, multi-purpose protection of main pipelines at higher protective potential, i.e. in places where other kinds of enamels are less effective.

This is the technique for preparing bitulene. Pulverized low-density polyethylene is mixed with bitumen at 140°C for 30 minutes. The polyethylene is gradually added to the bitumen during a continuous mixing process. Then the temperature is slowly (over a span of 20 minutes) increased to 160 - 180°C. Brief heating up to 200°C is permissible.

Bitumen-Polydiene-Polypropylene Enamel (BPP)

BPP enamel is chiefly notable for being obtained on a base of low-plastic bitumens.

Atactic polypropylene is used in the preparation of enamel; it is an intermediate product of the polymerization of propylene in the presence of a catalytic complex: triethylaluminum and titanium trichloride. The raw material for the manufacture of polypropylene is propane --the propenyl fraction of gases from thermal cracking. Attacking polypropylene is manufactured in the form of a clear, rubbery mass (volatiles content not more than 3%, ash content: not more than 1.5%, characteristic viscosity in decalins at 135°C is 100 milliliters/gram within limits of 0.4 - 1).

The enamel contains: up to 92% bitumen, 4 - 5% polydiene; 5 - 4% polypropylene. The enamel is obtained by steam-mixing the components (VTU-TNZ-171-66) at 190 - 210°C and admitting limited amounts of atmospheric oxygen. BPP enamel has a ring and ball softening point of 90°C, a needle penetration depth of 20 at 25°C, and an elongation of 1.5 cm.

* * *

The many formulations for enamel, and their properties and special features, make it possible to select enamels for specialized service conditions.

For example, the original type IV bitumen has a softening point of 72°C, whereas for operation under summer conditions an enamel with a softening point of not less than 80°C is required. After allowance for the effect of filler and plasticizer on the properties of the enamel, 9% rubber is introduced into the bitumen, which increases its softening point approximately 27°C, i.e. in this example from 72 to 99°C. Green oil (about 5%) is also introduced into the enamel to increase its plasticity, which lowers the softening point by approximately 20%. Thus the softening point is lowered by almost 20°C, down to 79°C, i.e., to the temperature required.

TABLE 37. RUBBER-BITUMEN ENAMELS

Temperature in °C		Physical and mechanical properties of enamels			Types of enamels
Ambient at time of application	Enamel when applied	R&B softening point in °C	Elongation in cm	Penetration in 0.1 mm	
From +5 to -30	From +150 to +180	65 - 70	4	40	MBR-IZ-65
From +15 to -15	From +150 to +200	71 - 75	4	30	MBR-IZ-75
From +30 to -15	From +160 to +200	80	4	30	MBR-IZ-80
From +35 to -10	From +160 to +200	90	3	20	MBR-IL-90
From +40 to -10	From +180 to +200	100	2	15	MBR-ILT-100
From +50 to -10	From +180 to +210	120	2	20	MBR-ITP-120

TABLE 38. POLYMER-BITUMEN INSULATING ENAMELS

Temperature in °C		Physical and mechanical properties of enamels			Types of enamels
Ambient at time of application	Enamel when applied	R&B softening point in °C	Elongation in cm	Penetration in 0.1 mm	
From +5 to -20	From +150 to +180	70	4	30	Bitudiene-70
From +30 to -10	From +180 to +200	80	2.5	20	Bitulene-80
		90	3	20	Bitudiene-90
From +35 to -5	From +160 to +200	90	2	15	Bitulene-90
		90	1.5	20	BPP

In selecting the formulations for enamels, technological requirements are the governing factor (Tables 37 and 38).

Tables 37 and 38 indicate that under winter conditions only plastic enamels with increased penetration should be used, or else brittle bitumens and refractory enamels should receive additional plasticization. The brittleness point of an enamel ultimately determines the minimum temperature at which insulated pipe can be laid in a trench.

Special attention must be paid to the temperature stability of coatings in choosing an enamel for service under summer conditions, especially in the southern regions of the country, and also in transporting the hot product.

CHAPTER THREE

COATINGS BASED ON SYNTHETIC RESINS

Unique exposed gas deposits in western Siberia and in the far North have provided a reliable source for further development of the gas-supply industry, power, and public and domestic consumption of gas in the European sector of the USSR.

Gas delivery is most efficient when large-diameter gas lines are used. However, because of their increased rigidity, such lines cannot very well follow the ups and downs of the terrain. They should therefore be suitable for underground as well as above-ground conditions. The complexity of assembling such pipelines and their great rigidity made it imperative to include in the first plan a factory-made insulation suitable for protecting pipelines from soil and atmospheric corrosion when they were laid underground, on the ground and above ground.

The large quantities of experimental data on protection of pipelines with rubber-bitumen against soil corrosion cannot be applied to the case of pipeline protection under atmospheric conditions.

The lack of coatings suitable for protecting large-diameter pipelines under both atmospheric and underground conditions has necessitated the solution of a large complex of problems: formulae for coatings made from synthetic resins had to be developed, their structural, mechanical and protective properties had to be studied, and technology and equipment for applying the insulation had to be developed.

These coatings are based on epoxy and furfuran resins, modified coal tar, polyester and polyamide resins, and certain synthetic rubbers. Epoxy resins are most often used for protective compositions, as they are the most reactive and conducive to obtaining coatings with specified properties for various service conditions.

Coal tar resin is used as a modifier, as the most effective and cheapest of available modifiers. This resin, moreover, also plays the role of a plasticizer in the composition.

Coatings based on synthetic resins are characterized by good structural and mechanical properties, high adhesion to metal, chemical stability to various corrosive media, resistance to heat and cold, ease of processing, and ability to harden at ordinary or slightly elevated temperatures (40 - 60°C). Such coatings can be painted onto the structures to be protected without the use of solvents, under stationary and field conditions, and will resist the corrosive factors found under both atmospheric and underground conditions.

The good structural, mechanical and protective properties of this form of insulation have enabled it to be applied directly at the pipeline factory. Because of the integrity and impermeability of these coatings, and their chemical stability, they can be applied 0.5 - 0.7 mm thick for exterior insulation and 0.3 mm thick for internal insulation. The high quality of the coatings makes it possible to dispense with cathodic protection, or to use it only for preventive treatment purposes.

The new coatings are more economical than those previously used to protect large-diameter pipes: the annual saving from the use of synthetic resin insulation in the laying of large-diameter pipelines amounts to about 2 million rubles.

Structural and Mechanical Properties of Coatings Based on Synthetic Resins

The physical and chemical parameters of polymer materials are governed by their rheological properties. Polymer materials do not obey the rheological laws of solid bodies, particularly Hooke's law. Thus, for example, an internal stress causes the phenomenon of both resilient and viscous deformations, the role of both being rather important.

The most important elements in the time dependence of deformation are the magnitude of the stress, the effective load time, the variation of properties with time after the load is removed, the rate of loading, and the temperature.

The curve of dependence of deformation on time can assume different forms, depending on the stress, temperature, actual period of load, molecular weight, and other factors; these also govern the complexity of the phenomenon of deformation of a polymer. The study of polymers in pure form therefore presents major difficulties. If the polymer sample is deformed at a constant stress, highly elastic and irreversible plastic deformations develop simultaneously in it. Deformation of polymers due to relaxation takes place with time: the deformations increase in proportion to the increase in the period during which the force is applied. In any given determination of highly elastic and plastic deformation, there is some question as to whether true polymer flow, or a highly elastic deformation relaxation process is occurring when an external force is applied.

Studies of coatings based on synthetic resins have demonstrated the good structural and mechanical properties of these materials.

Resilient, elastic and plastic deformation of polymer materials have been studied according to a method of constantly applied stress which was developed by Academician P. A. Rebinder. The method is based on the theory that there are three components to the deformation of materials: ϵ_0 - resilient deformation; ϵ_m - total value for resilient and elastic deformation; $\epsilon_m - \epsilon_0$ - elastic deformation. Stationary (or relaxation) flow $\frac{d\epsilon_{\text{residual}}}{dt}$ of the material occurs simultaneously, and its rate is constant from the very beginning of the experiment.

The quality of the apparent residual deformation can vary considerably, depending on compression conditions (period of load application, time of removal of load, temperature).

After stress is applied, there is an initial, magnitude-reversible, resilient deformation ϵ_0 , followed by highly elastic deformation ($\epsilon_m - \epsilon_0$), or resilient residual deformation, also mechanically reversible in magnitude, but developing gradually in time.

The rate of relaxation flow of the material is easily determined by the slope of part of the curve of deformation build-up. The section cut off on the ordinate by extending the linear part of the flow determines the maximum resilient deformation, allowing for total distribution of elastic deformation.

If the stress is quickly relieved, resilient deformation disappears at once. After that residual resilient deformation gradually disappears, whereas any deformation caused by flow of the substance is irreversible.

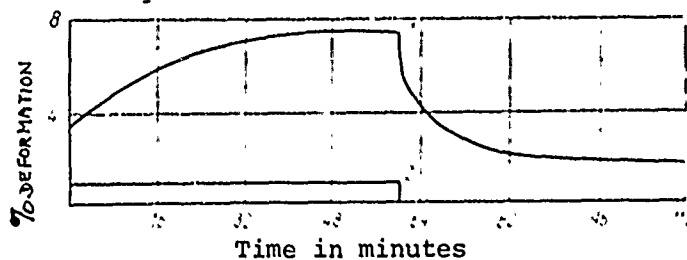
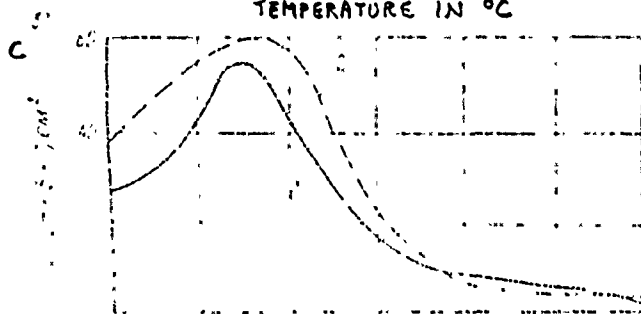
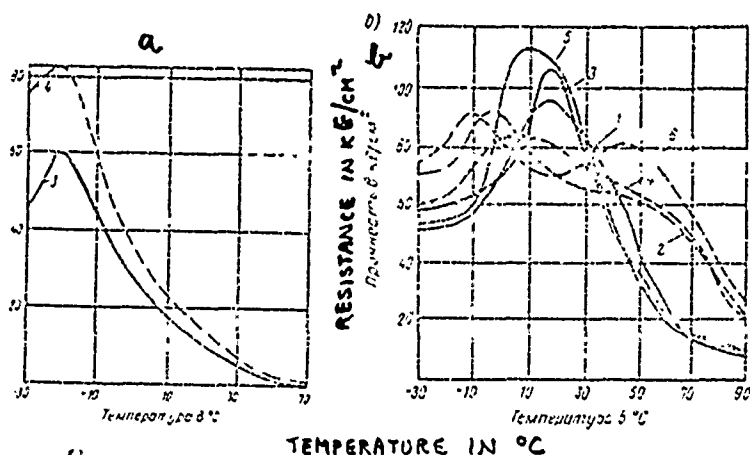


Fig. 22. Deformation of samples hardened by different methods
1 - cold; 2 - hot

Deformation curves are of identical nature, each consisting of the following parts:

- deformation caused by interaction forces of neighboring molecules and change of shape of molecules;
- residual resilient deformation caused by change of shape of polymer molecules under applied stress;
- the corresponding linear portion of the curve of plastically malleable irreversible deformation, representing steady-flow deformation which occurs when the load is applied.



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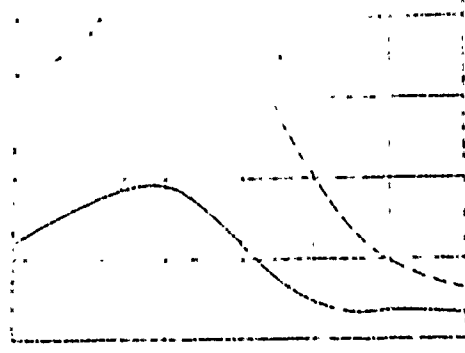


Fig. 23. Dependence of adhesion-cohesion stability on temperature. a - compound 53; b - compound 89; c - compound 45; d - compound 36; 1, 2 - one day; 3, 4 - three days; 5, 6 - ten days of curing. — cold hardening; - - - - - hot hardening.

In deciding the suitability of a composition for anti-corrosion protection of pipelines, one of the basic criteria is elasticity and plasticity of the coatings. The basic reasons for disintegration of coatings are their decrease in elasticity and their brittleness. Under certain conditions polymer materials inherently possess a highly elastic state. This is explained by the flexibility of their macromolecules, which are long chains composed of atoms joined by valence bonds of atomic interaction. The imposition of a deforming force causes directional variation of the shape of molecular chains;

they are able to oscillate or rotate around the bonds without disrupting valence forces.

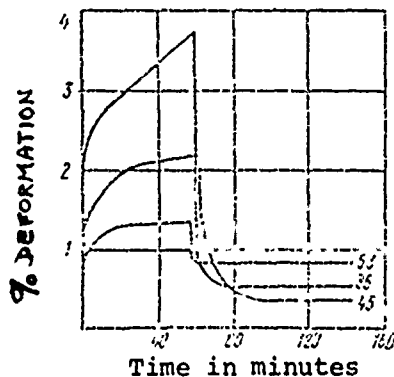


Fig. 24. Rheological diagram of compounds 36, 45, and 53, all of them cold-hardened

Fig. 22 shows deformation curves for samples hardened by different methods. Hot hardening gives a more rigid system, with decreased elastic properties; in cold hardening the compound can undergo transitory resilient deformation which is reversible in magnitude; spread of elastic deformation is also observed. The linear portion of the section confirms the presence of irreversible deformation due to viscous flow.

Research into the properties of the formulations developed has shown that the compounds which are in practice designated as 36, 45, 53, and 89 are optimal in basic rheological (and also protective) properties. These compounds have good physical and mechanical properties (Table 39). Adhesion value reaches a magnitude of more than 100 kg/cm^2 (compound 89); impact resistance in the majority of cases goes to $85 \text{ kg} \cdot \text{cm/cm}^2$ (depending on temperature); water-saturability falls within admissible limits. Figs. 23 and 24 show some structural and mechanical properties of the compounds.

Protective Properties of Coatings Based on Synthetic Resins

Protective properties of coatings are judged mainly by change in electrical resistance, diffusion constant, resistance to chemical media and micro-organisms, and resistance of the composition to thermal breakdown.

Electrical resistance and dielectric loss tangent. Knowing the protective properties of coatings, especially the manner in which these properties vary with elapsed time in a corrosive medium (the ground), makes it possible to estimate the quality and degree of protection of a pipeline not only for the initial construction period, but also for the service period, and also makes it possible to predict, however approximately, the service life of coatings under specific conditions. The basic reason for putting a protective coating on an underground pipeline is to insulate the pipe surface completely from a corrosive medium. Any protective coating should possess integrity. An unbroken coating implies not only the absence of defects, but also the absence

TABLE 39. PHYSICAL AND MECHANICAL PROPERTIES OF OPTIMAL COMPOUNDS FOR COATINGS
BASED ON SYNTHETIC RESINS

Com- pound	Har- den- ing	Adhesion- cohesion stability*			Impact re- sistance in kG·cm/cm ²			% water-saturability												Modu- lus of res.	Modu- lus of elas.
								Time in days						Time in months							
		3	10	30	3	10	30	3	6	9	12	18	14								
36	cold hot	60	74	-	70	75	75	0,51	1,16	2,11	3,2	4,5	5,4	6,3	7	8,6	0,03	0,3			
		100	92	-	85	85	85	0,42	0,98	1,72	3,5	4,9	6	6,5	8	8,9					
45	cold hot	20	36	-	55	60	67	0,23	-	0,48	0,73	0,88	0,88	0,9	0,9	1	0,14	0,23			
		41	44	-	85	85	85	0,32	1,01	2,55	4	4,5	4,7	5	4,7	4,8					
53	cold hot	13	25	36	185	85	85	0,53	0,95	2,54	5,15	7,2	9,7	11,2	14,6	16,5	0,33	0,26			
		27	45	45	85	85	85	0,71	1,29	3,51	6,25	9,3	12,2	13,4	17	18,1					
89	cold hot	90	70	80	65	85	60	0,3	0,57	1,01	1,9	3,9	4,1	-	-	-	0,94	0,34			
		103	91	80	85	85	85	0,27	0,52	0,95	1,81	3,24	4,1	-	-	-					

*properties determined at the base layer

of pinholes offering the corrosive medium a route to the metal. An unbroken coating depends for the most part on the structural and mechanical properties of the material in the coating, and the techniques used in applying it.

Integrity of a coating can be estimated by means of a high electrical current going from corrosive medium to coating to metal. Macroporosity can be determined by a defectoscope.

The integrity of the coating is basically determined by the care with which it is applied. Longevity implies maintenance of protective properties of the coating over a lengthy period of time. Longevity is primarily determined by the stability of the structural, mechanical, and physical properties of the material, the resistance of the coating to mechanical and physical effects, and the care with which the coating is applied.

The coating can undergo aging under service conditions, i.e. its physical and chemical properties can vary due to the effect of the medium surrounding it. Aging of coatings leads to impairment of their continuity and integrity.

Under certain service conditions, the water-proofness and water-saturability of a coating are important factors in its protective capabilities and longevity.

The electrometric method permits comparatively rapid estimation of the protective properties of a coating. An insulating coating containing a small amount of water or electrolyte has a high resistivity (10^{14} ohm · cm - 10^{12} x 10^{12} ohm · cm), which is usually decreased in accordance with the degree of water-saturation of the coating.

The various formulations for coatings based on synthetic resins offer high resistance to corrosive media. For example, a coating of compound 36 demonstrated high and stable resistivity, equal to 10^{12} ohm · cm, over 150 days of experiments. The dielectric loss tangent of this coating is about 0.02 - 0.03.

The coating made from compound 45 also has high dielectric properties (tested for 180 days), the resistivities for coating thicknesses of 1 and 2 mm being close to each other (about 10^{11} ohm · cm).

Coatings from compound 89, in different thicknesses (1 and 2 mm), retained high protective properties after two years of tests: their resistivity over that period was equal to 10^{11} - 10^{10} ohm · cm, and the dielectric loss tangent was 0.02 - 0.04.

Research shows that regardless of the method of hardening used, the best epoxy coating compounds have stable protective properties when kept in a corrosive medium for long periods.

Determining diffusion constants. Polymer coatings offer a fixed barrier to substances causing corrosion of metal.

A good idea of the probable performance of organic coatings under extended testing in a moist atmosphere can be obtained by determining the diffusion constants: the diffusion coefficient D , the coefficient of water permeability P (in $\text{g}/\text{cm}^2 \cdot \text{hours}$, mm Hg st), the coefficient of solubility of water in organic materials h (in g/cm , mm Hg st), and the equivalent quantity of water at saturation Q (in grams).

More exact determination of an assemblage of properties can be obtained by using the sorption method, based on solving a second Fickian diffusion equation for the nonstationary state of the process

$$\frac{dc}{dt} = D \frac{d^2c}{dx^2}$$

where c is the concentration of the medium at a distance x over a time t (water diffusion occurs in one direction), and D is the coefficient of diffusion (determining the rate of the sorption process) in cm^2/hour or cm^2/sec .

Measuring the diffusion constants of materials by the dynamic sorption method amounts in practice to determining the absolute weight increase of a dry sample Q_1 and Q_2 when it is in a wet medium.

To determine the characteristics P , D , h and Q , coatings are subjected to the action of a medium with a different relative humidity and chlorine ion content. The quantity of gases absorbed is determined by gravimetric means.

Table 40 shows results of tests on several coating formulae made out of synthetic resins; it follows from the table that the protective properties of coatings are adequate, in regard to moisture-resistance of the optimal

TABLE 40. DIFFUSION CONSTANTS OF COATINGS IN VARIOUS MEDIA

Compound	D, cm ² /hour	Q, g	h, g/cm mm Hg st	P, g/cm ² · hour, mm Hg st
IN HCl VAPOR				
45	$0.58 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$0.39 \cdot 10^{-3}$	$2.26 \cdot 10^{-6}$
89	$0.29 \cdot 10^{-2}$	0.59	$9.9 \cdot 10^{-3}$	$2.9 \cdot 10^{-5}$
87	$0.9 \cdot 10^{-2}$	0.21	$0.3 \cdot 10^{-2}$	$2.7 \cdot 10^{-5}$
AT 98% HUMIDITY				
45	$19 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$0.6 \cdot 10^{-3}$	$1.14 \cdot 10^{-6}$
89	$0.46 \cdot 10^{-2}$	$1.7 \cdot 10^{-2}$	$1.5 \cdot 10^{-2}$	$6.9 \cdot 10^{-5}$
87	$0.29 \cdot 10^{-2}$	$2.9 \cdot 10^{-2}$	$2.8 \cdot 10^{-2}$	$8.9 \cdot 10^{-5}$
AT 72% HUMIDITY				
45	$0.85 \cdot 10^{-3}$	$6 \cdot 10^{-2}$	$6.9 \cdot 10^{-2}$	$5.9 \cdot 10^{-5}$
89	$0.27 \cdot 10^{-3}$	$15 \cdot 10^{-2}$	$1.4 \cdot 10^{-3}$	$3.8 \cdot 10^{-7}$
87	$0.13 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$	$3.2 \cdot 10^{-2}$	$4.2 \cdot 10^{-5}$
IN WATER				
45	$0.12 \cdot 10^{-3}$	$1.7 \cdot 10^{-2}$	$0.6 \cdot 10^{-3}$	$0.72 \cdot 10^{-7}$

compounds. The values of diffusion constants D, h and Q amount to 10^{-2} - 10^{-3} ; the value of P lies within the limits of 10^{-5} - 10^{-7} .

Chemical and microbiological stability of coatings. The internal insulation of pipelines is also of great importance. The internal surfaces of metal pipelines are insulated in order to increase the service life of these structures when they are used to transport corrosive liquids and gases, and in order to increase pipeline capacity. Corrosive compounds contained in the products being transported interact with the metal to form corrosion pits and other defects. When paraffin oils are transported in the pipe (as in the petroleum industry), paraffin hydrocarbons are deposited on the walls of the pipes, leading to a sharp deterioration of the hydrodynamic characteristics of the pipes, increased expenditure of energy on transporting products, and loss of liquids and gases due to leakage. The coatings used to protect the internal surfaces of pipelines should be resistant to the action of various

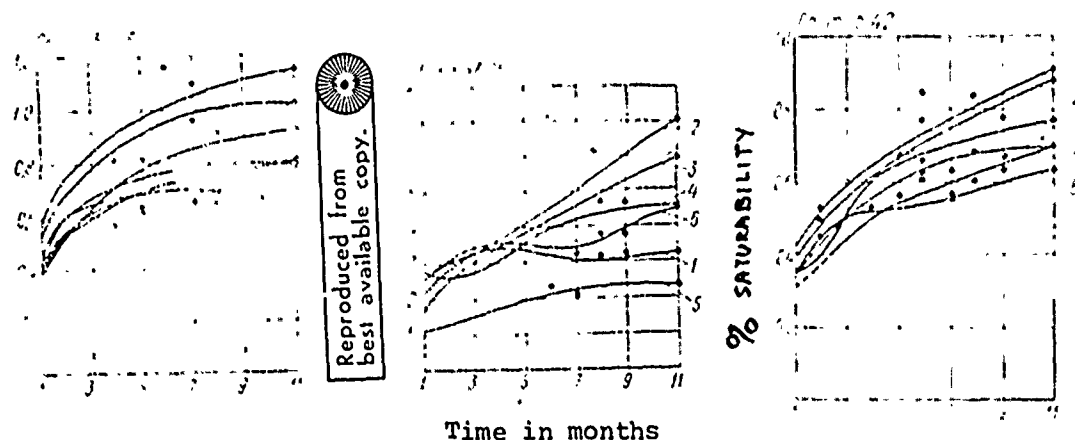


Fig. 25. Chemical stability (saturability in various media) of epoxy-coal-tar coatings.

media. The lack of chemically stable materials in easily processed proportions accounts for the fact that in numerous instances the internal surfaces of pipelines are not insulated. Internal insulation for pipelines should be resistant to various chemical media. A smooth surface sharply reduces deposition of paraffin hydrocarbons and increases the carrying capacity of delivery conduits.



Fig. 26. Fungus-resistance test on sample of compound 89

Epoxy-coal-tar and furfural-epoxy coatings can be used for internal insulation of pipelines. These coatings are chemically resistant to numerous media. As an example, Fig. 25 shows results of a study on the chemical resistance of coatings in solutions of sulfuric acid (curve 1) and hydrochloric acid (curve 2), sodium hydroxide (curve 3), sodium carbonate (curve 4), sodium chloride (curve 5), and hydrogen peroxide (curve 6).

From Fig. 26 it follows that coatings made of synthetic resins are resistant to the action of microorganisms (mold did not grow on the samples).

Resistance of coatings to oxidants. Many authors concede that oxygen and elevated temperatures are the basic factors causing aging of polymers. A quantitative allowance for these factors makes it possible to predict the service life of the coating and its thermal stability under specified temperature conditions. The effect of high temperatures is seen in the destruction of high-molecular-weight compounds, accompanied by a change in molecular weight and the formation of new structures.

The rate of oxidizing destruction also depends on the composition of the polymer. In a number of cases a thermal method of oxidizing materials in a medium saturated by oxygen is used to estimate the longevity of polymers. This method simulates the process of natural aging of polymers due to temperature and oxygen.

A method of oxidizing destruction in an oxygen medium suggested by L. G. Angert also makes it possible to predict how polymer materials will age naturally. In this method the rate of aging of polymers is studied in a micro-oxidizing apparatus (Fig. 27) comprised of two parallel oxidizing systems and two ovens. A specified temperature is maintained by means of contact thermometers. The entire apparatus is evacuated, and then oxygen is admitted.

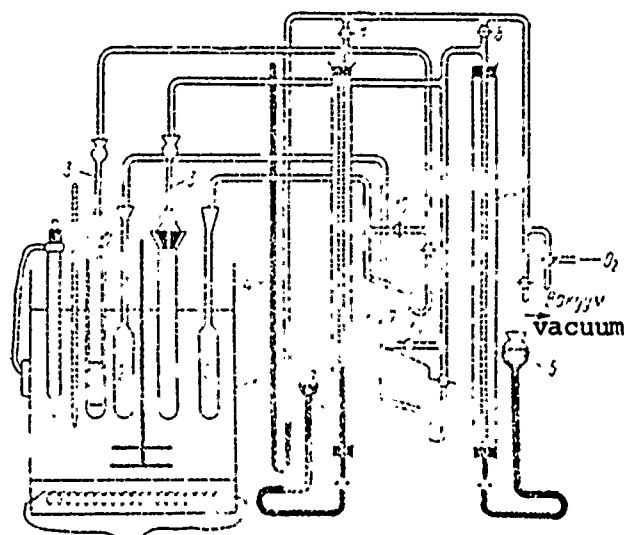


Fig. 27. Micro-oxidizing apparatus. 1 - oven for maintaining specified temperature; 2 - barostat volume (equalizes pressure in system); 3 - reaction vessel; 4 - manometer; 5 - bulb with mercury; 6 - microburet; 7 - Huygens manometer (regulates movement of oxygen in system); 8 - 10 - two-way stopcocks

By means of a microburet the quantity of oxygen absorbed by the material during a specified period is determined, and this is used to calculate a constant reaction rate. The apparatus permits detection of as little as 0.01 ml absorbed oxygen.

The amount of oxygen absorbed per 1 gram of substance is calculated according to the formula

$$\frac{V_0 P_0}{T_0} = \frac{V_1 P_1}{T_1}$$

where P_0 is normal atmospheric pressure (760 mm Hg st); V_0 and V_1 are the volume of absorbed oxygen in ml before and after the test, respectively; T_0 is the absolute temperature (273°C); P_1 is atmospheric pressure at the time of the test in mm Hg st; T_1 is the absolute temperature of the surrounding medium in °K.

The specific volume of oxygen absorbed is computed by the formula

$$V_0 = \frac{P_1 V_1 T_0}{P_0 T_1 g} \quad \text{ml/g,}$$

where g is the weight of the test sample in grams.

The resistance of a polymer to thermal destruction is determined by the duration of the induction period, i.e. the time elapsed from the moment the material is mixed in the test medium by a given method up to the onset of oxidation (beginning of absorption of oxygen).

Research into the reaction rate of oxidation of various polymers in dependence on the temperature of the experiment has made it possible to establish the temperature ranges of the oxidation process of the materials studied within limits of 100 - 200°C. It has been established that at 100°C the oxidation process proceeds slowly; it therefore requires long-term observations; at 200°C it occurs too fast and therefore hampers observations. The most favorable temperature for research is one in the range from 150 to 160°C.

The reaction rate constant is determined as the ratio of the volume of absorbed oxygen to the time of the induction period of oxidation at various temperatures. As an example, Table 41 shows oxidation rate constants for compound 53.

TABLE 41. OXIDATION RATE CONSTANTS OF COMPOUND 53

$T^{\circ}K$	$\frac{1}{T}$	k_T	$\lg k_T$
293	3.4	0.09	-1.047
313	3.2	0.186	-0.73
333	3.1	0.354	-0.451
353	2.8	0.402	-0.395
393	2.5	1.05	0.211
413	2.4	1.811	0.256
433	2.3	2.257	0.352
453	2.2	3.11	0.493

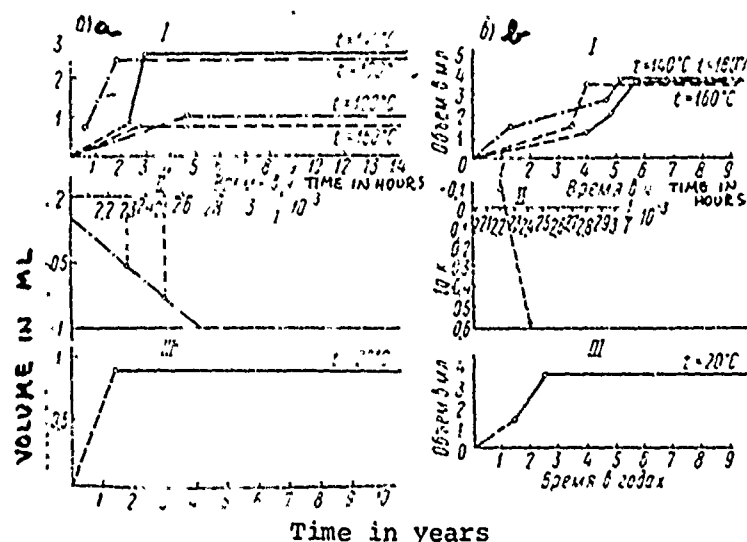


Fig. 28. Reaction rate constants. a - compound 45; b - compound 89; I - dependence of value of oxygen absorption on time at various temperatures; II - dependence of reaction rate constant on inverse value of absolute temperature (determination of K for various temperatures); III - dependence of oxygen absorption value on time at 20°C

Individual characteristics can be determined from data on the reaction rate constant at two temperatures (for example, 80°C and 120°C).

According to data from full-scale studies, the underground service life of bitumen coatings modified by polymers amounts to about 25 - 30 years; under atmospheric conditions many of them are unstable. This is confirmed by data shown in Table 42 and in Fig. 28, which attest to the longevity of epoxy-coal-tar coatings.

TABLE 42. OXIDATION RATE CONSTANTS

Material	Temperature in °C							
	210	180	160	140	120	100	40	20
Oil bitumen III	11.05	10.1	8.5	5.1	-	3.56	1.24	0.745
" IV	11.5	8.9	8.2	5.1	4.46	3.54	0.637	0.457
" V	16.1	-	8.7	-	-	3.04	0.562	0.342
Bitumen-poly-ethylene enamel	13.5	7.96	6.25	5.02	3.98	2	0.994	0.447
Epoxy-coal-tar compound 45	-	-	-	5.8	-	2.2	-	0.00079

A summary of the properties of coatings made of synthetic resins shows their suitability for external and internal insulation of pipelines and for use under underground and atmospheric conditions. The main properties of the coatings are given below.

Basic Properties of Epoxy-Coal-Tar Coatings

% water absorption	
1 day	0.3
30 days	0.7
Coefficient of diffusion at 98% humidity in cm ² /hour	$0.29 \cdot 10^{-2}$
Equilibrium quantity of moisture at saturation in grams	$1.7 \cdot 10^{-2}$
Coefficient of water permeability in g/cm·hour mm Hg st	$2.26 \cdot 10$
Coefficient of dissolved moisture in g/cm ³ mm Hg st	$0.3 \cdot 10^{-3}$
Impact resistance in kG/cm/cm ²	85
Adhesion to metal in kG/cm ²	80
Modulus of resilience in kG/cm ²	$0.94 \cdot 10^5$
" elasticity in kG/cm ²	$0.33 \cdot 10^5$
Microbiological properties:	
stability	stable
fungus-resistance for 3 and 40 days (estimated fungus growth on 6-intensity system)	0
Volume resistivity in ohm · cm:	
initial	10^{11}
after 2 years in a corrosive medium	10^{10}
Dielectric loss tangent	0.04
Value of breakdown voltage in kv	36
Thermal stability in °C	+70
Frost stability in °C	-60

Density in kg/dm ³	1.4
Reaction rate constant K at 20°C	$2.7 \cdot 10^{-4}$
% shrinkage	$9.4 \cdot 10^{-4}$

Formulating a Composition

The Effect of the Formula of a Composition on its Properties

The processibility of new coatings and the ease of obtaining and applying them make it possible to use them under a variety of conditions. It is therefore especially important to decide upon a formula for the composition needed, since the formula will determine the properties and areas of applicability of the material.

Besides resins, fillers, plasticizers and hardeners are also part of the formula for a composition.

In most instances epoxy resins are used with various mineral fillers. Because of the high adhesion of epoxy resins to mineral substances, after hardening monolithic compositions are formed which have good physical and mechanical properties and chemical stability. Often used as a filler are marshallite, ground porcelain, alumina, ground asbestos, cement, talc and graphite. Table 43 and Fig. 29 show the durability properties of coatings in dependence on the kind and amount of filler used.

From Table 43 it follows that compounds without fillers are more elastic. This rule holds true for the different methods of hardening.

In selecting a filler, its effect on the degree of abrasiveness of the compound must be allowed for. If the original compound is slightly reinforced

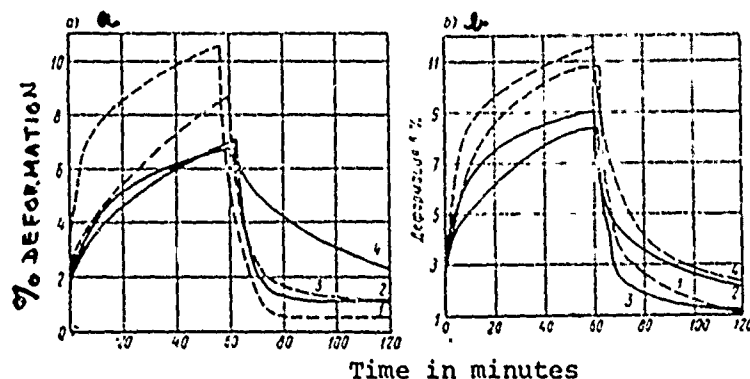


Fig. 29. Rheological diagrams of deformation of composition in dependence on presence of filler. a - compound 59; b - compound 60; 1, 2 - cold hardening; 3, 4 - hot hardening; 1, 3 - without filler; 2, 4 - with filler.

by any kind of mechanical processing, then the reinforced compound, depending on the nature of the filler, may have a high degree of abrasiveness.

TABLE 43. SHEAR STRENGTH OF EPOXY COMPOUNDS

	Temp. of experiment in °C	Limit of shear strength in kg/cm ² at a filler content, in %, of					
		0	5	10	15	20	30
Ground asbestos	20	275	360	435	315	280	260
	120	220	260	295	260	240	225
Ground silica gel	20	275	-	315	-	250	-
	120	220	-	245	-	210	-
Marshallite	20	275	-	300	-	390	380
	120	220	-	-	-	230	250

Note: dicyandiamide used as hardener.

The amount and kind of filler added to the resin differ greatly, depending on the purpose and properties of the compound. The maximum limit for filler can go to 200% (with no solvents in the composition). The introduction of such a filler as pulverized talc in amounts greater than 130% is already difficult because of the high viscosity of the composition which results.

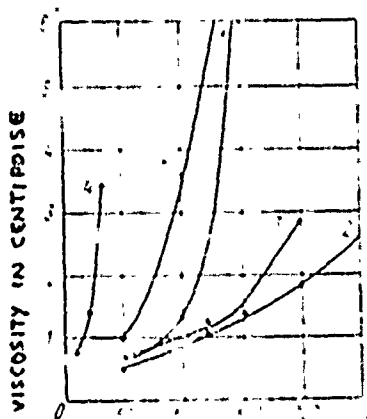


Fig. 30. Dependence of viscosity of compound on type and amount of filler. 1 - talc; 2 - pulverized diabase; 3 - sand; 4 - ground asbestos; 5 - kaolin

Fig. 30 shows viscosity curves of compounds with fillers added, from which it is evident that compounds with ground asbestos have the greatest viscosity, and those with pulverized diabase have the least. During preparation of the composition, the viscosity of the mixture is increased more rapidly for compounds with pulverized asbestos, kaolin and talc, and more slowly for compounds with sand and pulverized diabase. Maximum filling can be permitted in individual cases, if a viscosity suitable for processing is maintained (for example, equal to $2.85 \cdot 10^5$ centipoise for epoxy-coal-tar coatings).

Ground asbestos is used in 30 parts by weight to 100 parts by weight of ED-5 resin, kaolin in 90, talc in 130, sand in 200, and pulverized diabase in 250.

TABLE 44. PHYSICAL AND MECHANICAL PROPERTIES OF COMPOSITIONS WITH VARIOUS FILLERS

Filler	Amt. filler	$\eta, 10^5$ centi-poise	Adhesion-cohesion stability* in kg/cm^2 for number of days			Impact stability* in $\text{kg}\cdot\text{cm/cm}^2$ over number of days			% water-saturability over number of days		
				10	30	3	10	30	3	10	30
Talc:	50 parts by wt										
calcined		0,4	30	31	37	45	40	60	0,38	0,57	0,8
non-calcined		0,6	17	20	35,7	85	75	65	0,30	0,36	0,46
Pulverized diabase		0,56	21	39	—	55	45	85	0,33	0,44	0,61
Sand		0,61	17	21	28	45	40	50	0,24	0,39	0,62
Kaolin		1,01	21,5	25,7	47	55	45	30	0,33	0,57	0,89
Calcined talc	100 parts by wt	2,57	30	41	66	65	65	60	0,5	0,48	0,72
Pulverized diabase		—	19	25	41	85	55	50	0,15	0,26	0,45
Sand		—	24,5	50	50	45	40	25	0,11	0,2	0,28
Kaolin		—	17	53	60	45	45	50	0,11	0,19	0,31

* properties determined at the base layer.

Table 44 shows the properties of coatings with various fillers, and Fig. 31 the dependence of adhesive-cohesive stability upon duration of hardening (at 20°C) and on type and amount of filler. From Fig. 31 it follows that compounds containing 100 parts by weight of kaolin have the greatest stability, and those containing 50 parts by weight of sand have the least.

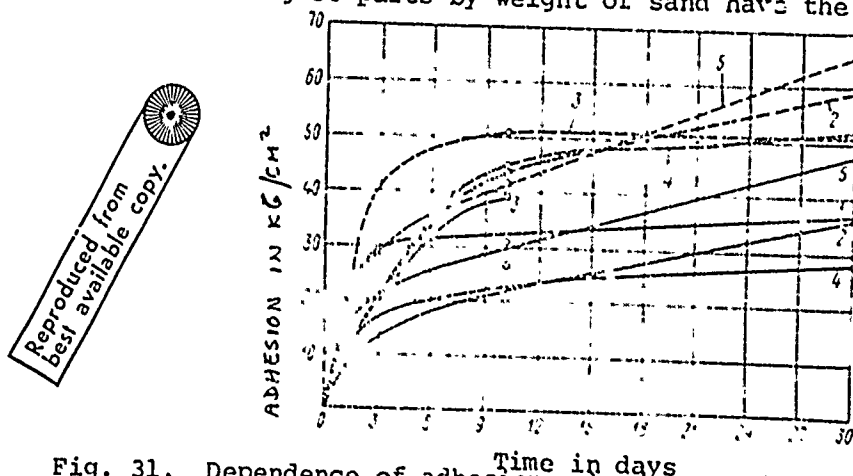


Fig. 31. Dependence of adhesion-cohesion stability on time. 1 - calcined talc; 2 - non-calcined talc; 3 - pulverized diabase; 4 - sand; 5 - kaolin; — 50 parts by weight of filler; - - - 100 parts by weight of filler

An important characteristic for estimating the effect a filler will have on the properties of coatings is the water-saturability of the compounds. From Fig. 32 it follows that the water-saturability of the compounds is very slight. Over a period of months the maximum water-saturability does not exceed 1%. Of the fillers mentioned, that having the least water-saturability (0.46% per month) is non-calcined talc, and that having the most (about 1% per month) is kaolin, when they are added to compounds. The type and quantity of filler introduced are determined by a number of conditions: reduction of the coefficient of linear expansion to a specified value; increase of thermal stability; increase of mechanical stability; provision of necessary fluidity; uniform distribution of filler throughout the whole volume of the compound. Depending on the weight and amount of filler, and also the viscosity of the resin, the agglutination observed will be greater or less. Whenever large-scale structures are to be insulated, filler should be introduced into the coating compound. Only when lesser volumes of metal are involved and internal pressures are negligible can a plasticized compound be used without filler added to it.

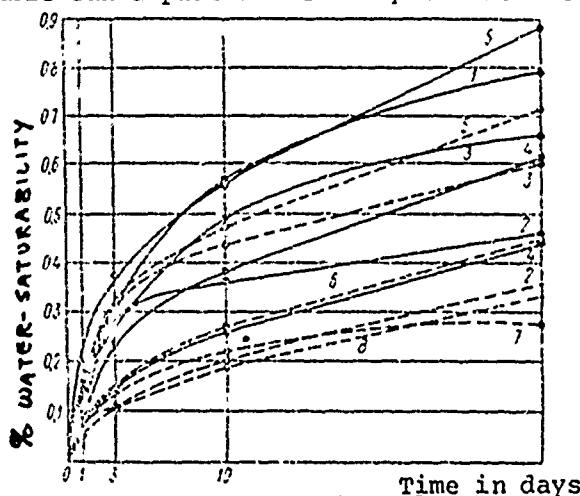


Fig. 32. Dependence of water absorption of polymer compounds on type and amount of filler. 1 - calcined talc; non-calcined talc; 3 - pulverized diabase; 4 - sand; 5 - kaolin; (— 50 parts by weight of filler; -----100 parts by weight of filler); 6 - non-calcined talc - 130 parts by weight; 7 - pulverized diabase - 260 parts by weight; 8 - sand - 200 parts by weight.

Plasticizers are introduced into epoxy compounds in order to reduce their brittleness: low-molecular-weight synthetic rubbers, coal-tar resin, dibutylphthalate, tricresolphosphate. Plasticizers are added to amounts of 15 - 20% of the weight of the resin. Exceeding these limits leads to a loss of quality in the hardened compounds. Coal-tar resin is most often used as a modifier (and plasticizer) of epoxy compositions.

Epoxy-coal-tar compositions were created to meet the need for coatings with high structural and mechanical properties in the temperature range from +90 to -60°C.

Epoxy-coal-tar compositions with a different coal-tar resin content are of great interest. The principal hardener for these compositions is polyethylene or polyamide. A filler is also part of their composition. This

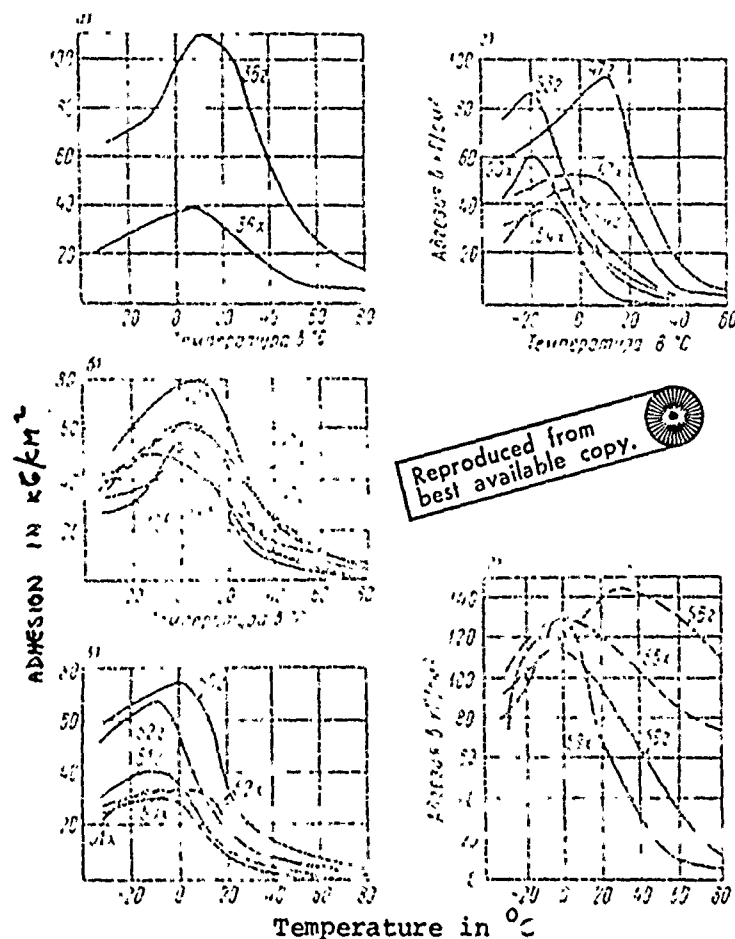


Fig. 33. Dependence of steel adhesion of polymer compositions on type of plasticizer with different hardening methods (x - cold; g - hot). a - thiokol; b, c - coal-tar resin; d - FA monomer; e - aliphatic epoxy resin.

composition does not contain a solvent. Hardening can be done at various temperatures (from room to 80°C).

Fig. 33 shows the effect of coal-tar resin on the adhesion-cohesion stability of compositions. The comparison of the properties of epoxy-coal-tar-thiokol and epoxy-thiokol compositions confirms the reduction of cohesion properties of coatings when coal-tar resin is introduced. Nevertheless, the stable properties of the epoxy-coal-tar coatings seem good.

Formulations for epoxy-coal-tar-thiokol compositions are numerous, thanks to the availability of several kinds of epoxy resins, and the variety of hardeners and addition agent compounds available to be added to them. The compounds shown in Table 45 have the best properties.

Adding aliphatic epoxy resin (AER) to epoxy-coal-tar compositions in the amount of 20 parts by weight significantly increases the structural and

TABLE 45. FORMULATIONS FOR EPOXY-COAL-TAR-THIOL COMPOSITIONS (IN PARTS BY WEIGHT) BASED ON ED-5 RESIN

Constituent	No. of compound							
	42	45	49	50	51	52	36	69
ED-5 epoxy resin	100	100	100	100	100	100	100	100
Coal-tar resin	80	80	100	120	150	200	-	100
Talc	100	100	100	100	100	100	100	100
Polysulfide rubber (thiol)	-	20	20	20	20	20	20	-
Polyethylenepolyamine	10	10	10	10	10	10	-	-
L-18 Polyamide	-	-	-	-	-	-	80	80

TABLE 46. FORMULATIONS FOR EPOXY COMPOSITIONS (IN PARTS BY WEIGHT) MODIFIED BY FA MONOMER AND AER

Constituent	No. of compound							
	47	89	53	54	56	58	59	60
ED-5 epoxy resin	100	100	100	100	100	100	100	100
Talc	200	100	200	200	100	100	100	100
Polyethylenepolyamine	20	23	20	20	20	19	-	19
FA monomer	100	-	120	150	-	-	-	-
Benzenesulfonic acid	-	-	24	30	-	-	-	-
AER	-	20	-	-	20	20	20	20
Coal-tar resin	-	100	-	-	-	-	100	100

TABLE 47. FORMULATIONS FOR COMPOSITION (IN PARTS BY WEIGHT) BASED ON ED-6 EPOXY RESIN

Constituent	No. of Compound	
	62	65
ED-6 epoxy resin	100	100
Coal-tar resin	-	100
Talc	100	100
Polyethylenepolyamine	18	18
AER	20	-

mechanical properties of these compositions (Tables 46 and 47) --their impact resistance amounts to more than 85 kG/cm².

A comparison of compounds based on ED-5 and ED-6 resins shows that the adhesion-cohesion properties of compounds based on ED-6 resin are significantly higher than for compounds based on ED-5 resin; however, the latter is more processible, if it is considered that the composition is prepared without solvents. The properties of compound 62 are more stable with different hardening methods and are maintained over a wide temperature range. Thus, the value of the adhesion-cohesion stability of compound 62 in the temperature range from -50 to +90°C lies within limits of 70 - 130 kG/cm², whereas for

compound 65 the adhesion-cohesion stability drops sharply with increased temperature, approaching the minimal at 90°C. Comparing the properties of the coatings obtained with different hardening methods (cold and hot), it is easy to see that for compound 62 the maxima of curves are shifted slightly toward higher temperatures in the case of the hot method and toward lower temperatures in the case of the cold method.

The curves of the cold and hot hardening methods are close for compound 65. Considering Fig. 34, it can be seen that the dependence of adhesion stability on duration of hardening is identical (for 10 days and for 3 days). Over a shorter duration no such regularity can be detected, since the hardening process is not completed.

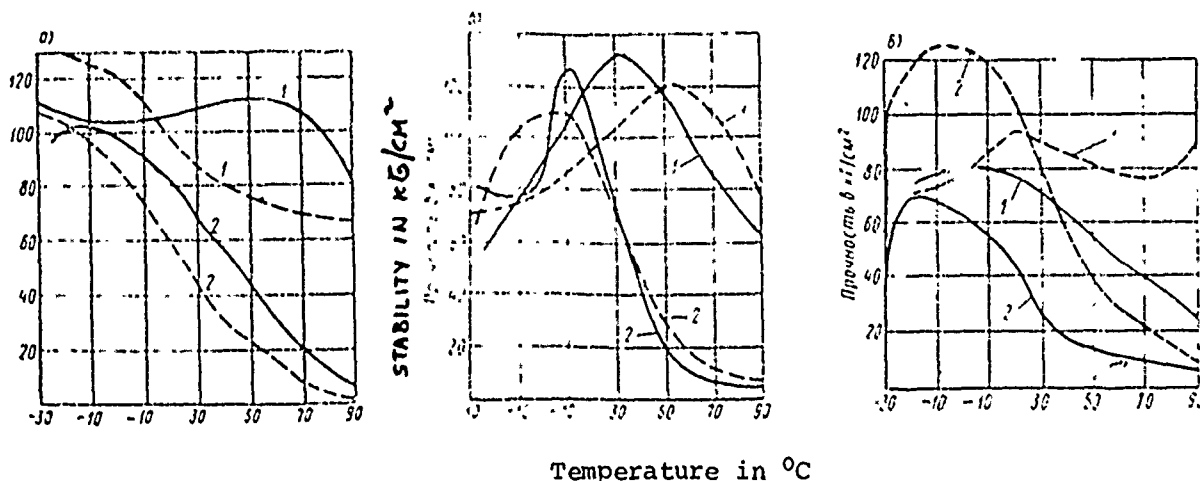


Fig. 34. Dependence of adhesion-cohesion stability of compounds 62 (1) and 65 (2) on duration of hardening. a - 10 days; b - 3 days; c - 1 day; — cold hardening; ---- hot hardening.

Insulating coatings based on epoxy resins, modified by various constituents, are obtained with the specified resilient and plastic properties with the use of different hardening methods.

Comparison of the deformation properties of enamels hardened by the hot and cold methods has shown that when a two-constituent plasticizer is used in the hot method, resilient and elastic properties are principally developed, whereas these properties are either not manifested at all, or are only slightly developed, with the cold method.

Compounds containing coal-tar resin, 42, 45, 49, 69 and FA monomer (compound 53) exhibited the presence of an assemblage of deformation properties; coatings based on compounds 36, 56 and 58 are more stable.

As the coal-tar content increases, the elasticity and deformability of the coating increase (Fig. 35).

Fig. 36's deformation curves of compounds 56, 58 and 59 show rather low elastic properties for epoxy compositions modified by aliphatic epoxy resins.

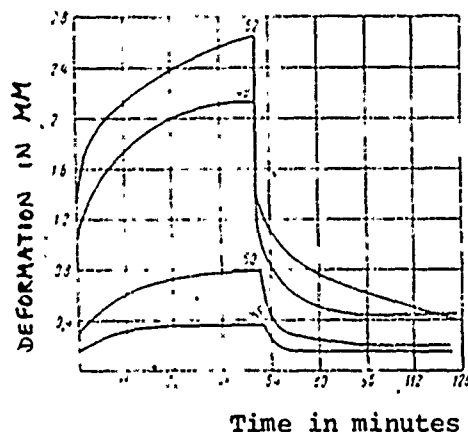


Fig. 35. Curves of deformation of samples of epoxy compounds modified by coal-tar resin

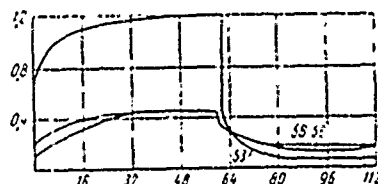


Fig. 36. Deformation curves of samples of epoxy compounds modified by DEG-1 and EFG

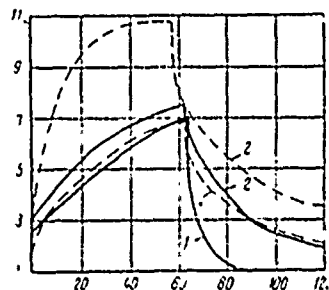


Fig. 37. Deformation curves of samples of epoxy compounds modified by DEG-1, EFG and coal-tar pitch. 1 - compound 59; 2 - compound 60; — cold hardening; ---- hot hardening

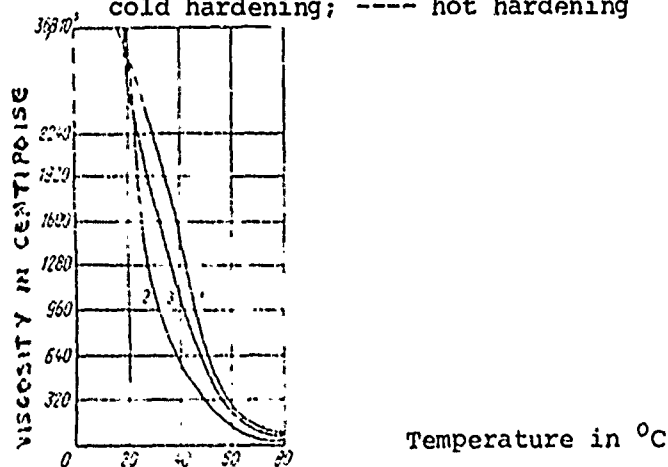


Fig. 38. Rheological curves of viscosity. 1 - ED-5; 2 - coal-tar pitches; 3 - mixtures of coal-tar pitch, thiokol and PEPA

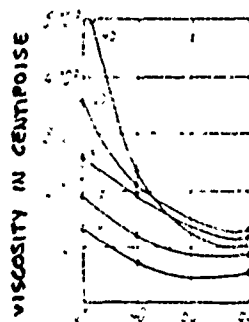


Fig. 39. Rheological curves of viscosity of compounds in dependence on quantity of coal-tar pitch

These compositions, additionally modified by coal-tar pitch (compounds 59 and 60), already have high enough elastic properties (Fig. 37).

One of the most important factors in processibility is viscosity. When substitutions of various constituents are made in coatings, it is necessary to have a clear idea as to how the viscosity of compounds changes in dependence on various factors, especially temperature. Fig. 38 gives curves of viscosity of ED-5 (1), coal-tar pitch (2), and compound 45 (3).

It is evident from the figure that at 60°C the viscosities of compound 45 and the epoxy resin are practically identical. This means that at a temperature of 60°C the correct proportion of constituents can be attained when the mixture and the resin flow in simultaneously from the mixers.

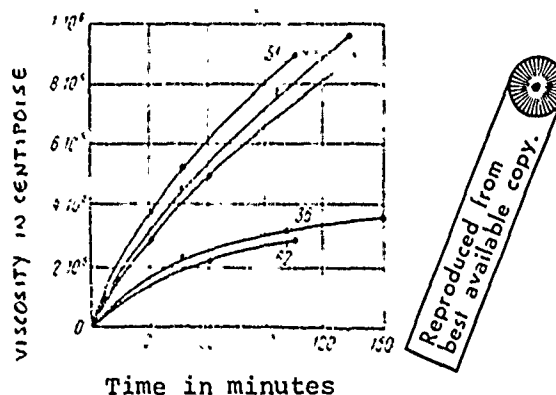


Fig. 40. Variation of viscosity of compounds in time from moment of introduction of hardener (36, 49, 50, 51, 52 - compound numbers)

The effect of the amount of coal-tar pitch on the viscosity of a compound is shown in Fig. 39. Decrease in viscosity is proportional to the amount of coal-tar pitch (with the exception of compound 45, which has additional plasticizer --thiokol). Thus by adding coal-tar pitch to a composition we are able to adjust the viscosity to a specified value.

The amount of coal-tar pitch used does not affect the rate of hardening of the composition. As is seen from Fig. 40, coal-tar-epoxy compounds 49, 50, 51, which differ in coal-tar pitch content (100, 120, 150 parts by weight),

behave quite identically. Thus in the two-hour period following introduction of a hardener, the compounds attain an identical viscosity of $9 \div 10 \cdot 10^5$ centipoise. Compound 52, containing 200 parts by weight of coal-tar pitch, seems more easily processed. Thus, in a period of one hour after introduction of the hardener, its viscosity reaches $2.5 \cdot 10^5$ centipoise. Compound 36 has a smoother plot of its curve of viscosity change.

Solvents are introduced into the formulation of epoxy compositions to decrease their viscosity at room temperature. The best solvents for epoxy resins are ketones, especially acetone. Low-molecular-weight diene epoxy resins are also soluble in aromatic hydrocarbons. Solvents blended from aromatic hydrocarbons, alcohols, ketones and complex esters are often used. Diene resins are insoluble in ethyl alcohol.

Active thinners are used in preparing compositions without solvents in order to decrease viscosity. Whereas the solvents are driven off during processing, the thinners remain, wholly or in part, forming a composition with the resin and the hardener. Low-molecular-weight, low-viscosity substances containing epoxy groups in their molecules are most often used as active thinners. Among such substances are styrylic oxide and allylglycidyl, butylglycidyl and phenylglycidyl esters. Also used as thinners are low-viscosity products containing two or more epoxy groups in their molecules, or products obtained from epichlorohydrin and poly aliphatic alcohols. Thinners usually have a somewhat deleterious effect on the properties of hardened epoxy compositions --they reduce the thermal stability, and decrease the hardness and modulus of resilience. However, in a number of instances the only way to obtain epoxy compositions with the necessary properties is to use thinners, as, for example, with cold-hardened compounds for insulating large expanses of pipeline metal.

Hardeners. Epoxy resins acquire industrial importance if they can easily be hardened, i.e. be brought out of the liquid or dissolved state and made refractory and insoluble. Many factors affect the properties of the final product: properties of hardening accelerators, properties of polyfunctional compounds causing cross-linking of molecules or groups, amount of hardener introduced, temperature at which hardening occurs, duration of the hardening process, and many others. Changes in the molecules and formation of cross-links are accompanied by a change in the physical, chemical, mechanical and electrical properties of the epoxy resins.

Depending on the kind and quantity of hardener introduced into the resin, thermo-reactive products may be obtained which differ in having high chemical and mechanical stability, and stable electrical properties.

The hardener selected depends on the purpose for which the composition is intended. If hardening must be completed quickly at normal temperatures, the acid hardeners are not usually used, since they require heat. Instead, amino compounds such as polyethylenepolyamine (PEPA), pyridine, hexamethylenediamine (HMD), vat residues and others are used.

The criterion for selection of a hardener is high stability of the composition under the temperature conditions to be imposed.

TABLE 48. CHANGE IN NOMINAL VISCOSITY OF EPOXY RESINS WITH DIFFERENT HARDENERS (HOT HARDENING)

Hardener	Amt. hardener by weight per 100 parts of resin	Nominal viscosity in sec at 80°C after being kept at room temperature for a period of (in hours)								
		0	24	48	72	96	120	148	172	198
Maleic anhydride	35	4	7	10	14	19	-	48	119	137
Pyridine	7	160	no flow	-	-	-	-	-	-	-
Hexamethylene tetramine	7	35	-	83	-	86	88	-	167	no flow

The stability of the composition will differ, depending on the type of hardener used, and the amount. Table 48, as an example, shows data on the change in viscosity of epoxy resins with various hardeners at 80°C in dependence on duration of storage at room temperature.

Temperature conditions during hardening exert a greater influence on the rate of hardening than anything except the nature of the hardener and its amount.

For convenience in selecting hardeners from among those most widely used, they are divided into two groups: hardeners requiring heat (maleic, phthalene, succinic anhydride, triethanolamine, dicyandiamide, mixtures of maleic and phthalene anhydride, urea-formaldehyde resin, phenolformaldehyde resin, et al.), and hardeners which can harden resins at room temperature (hexamethylene-diamine, polyethylenepolyamine, metaphenylenediamine, mixtures of amines, et al.).

The amount of hardener required in each individual case depends on the epoxy number of the resin, but it is not in equivalent ratio with the epoxy group.

The epoxy group content is computed according to the formula

$$X_e = \frac{(a - b) k \cdot 0.0043}{c} 100\%$$

where X_e is the epoxy group content in %; a is the number of milliliters of 0.1 normal solution of NaOH going into titration of a reference sample of hydrochloric acid with acetone; b is the number of milliliters of 0.1 normal solution of NaOH going into titration of a weighed portion of epoxy resin; c is the weighed portion of epoxy resin in grams; k is the coefficient of normality of the NaOH solution; 0.0043 is the amount of the epoxy groups in grams, corresponding to 1 milliliter of 0.1 normal NaOH solution.

The amount of hardener is computed by the formula

$$g = \frac{M_o}{M_e} k$$

where g is the weight of hardener per 100 grams of resin; M and M_0 are the molecular weights of the hardener and the epoxy group, respectively; k is the epoxy number of the given resin.

The amount of triethanolamine introduced into the resin should be many times less than indicated by computations, and is established experimentally.

Correct computation of the amount of hardener has a substantial effect on the final properties of the polymerized compound.

The reaction of polymerization of epoxy compounds with the alkaline hardeners proceeds faster than with the acid ones in the majority of cases, as has already been mentioned; therefore the polymerization temperature of the compounds is so chosen as to ensure fulfillment of technical requirements in relation to reactivity of the compound and the possibility of obtaining the necessary physical and mechanical characteristics.

The properties of hardened epoxy resins depend on the quantity of hardener added. This is especially so when the hardener is called for in small amounts (5 - 10 grams per 100 grams of resin). When polyethylenepolyamine is used as a hardener for ED-5, ED-6 and E-40 resins, too small an amount of it slows hardening and keeps it from being completed. Such a coating is chemically unstable; it is dissolved by organic solvents.

With an excess of hardener, a film appears on the surface of the hardened resin and the physical and mechanical properties deteriorate (water-proofness is decreased). Excess hardener inhibits hardening. In this case resin is observed to dissolve in the excess hardener. Addition products (adducts) of amines to the epoxy resin are formed, which make good hardeners for new batches of resin. They are obtained by mixing the epoxy resin with polyamine in a molecular ratio of 1 : 2 or 1 : 2.5.

Hardeners which require heat for their action are usually added to epoxy resins in the amount of 20 - 40%. They harden low-molecular-weight and high-molecular-weight resins equally well.

The process of modification affects the properties of hardened epoxy resin in different ways. The use of fatty acids for modification causes the formation during the hardening process of products which are less hard and less stable in their chemical relationships, because of the presence of complex bonds in them. Blending epoxy resin with organo-silicone and furilo-acetone resins makes it possible to obtain more heat-resistant hardening products.

Unadulterated and unplasticized epoxy compounds differ in brittleness, which, combined with the high coefficient of linear expansion natural to them ($\alpha = 65 \cdot 10^{-6}/^{\circ}\text{C}$), can create a serious obstacle to the use of such compounds for insulating structures made of metal, especially large ones.

Method for Determining Degree of Hardening of Epoxy Compositions

During hardening epoxy resins go through three stages: liquid, tacky, and hard. The degree of hardening of a composition is determined by the vibration method, by the adhesion-cohesion stability, or by refractometric means.

Evaluation of the process of hardening of coatings by a vibration method makes it possible to estimate the stage the composition has reached in transition from the liquid to the hard state. This method is based on the fact that as the compound hardens, its viscosity increases and the amplitude of oscillation of a vibrating rod placed in the compound being studied decreases.

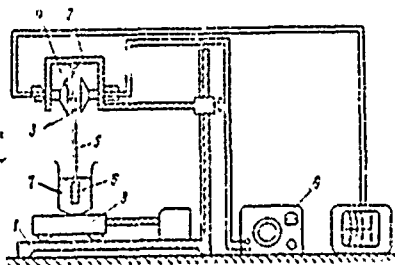


Fig. 41. Operating diagram of vibrometer

The vibrometer¹ (Fig. 41) consists of a frame 1 with a stand 2 mounted on it, on which is mounted the vibration element, consisting of two speakers. The cones of both speakers are joined together by a rigid pull rod 4, to which rod 5 is joined in a hinged manner; this rod has a special tip 6. The rod, immersed in the compound 7 to be studied, is set on a stand 8 which can automatically travel along the stand at a rate of 3 - 5 mm/hour. A voltage with a frequency of 400 hz is supplied to one of the speakers from a ZG-10 type signal generator 9. Vibration of the speaker causes horizontal oscillation of the rod. By means of a rigid rod, the vibration of the rod is imparted to the cone of the second speaker element. The emf induced in the latter's coil is proportional in magnitude to the amplitude of oscillations of the rod. The emf is recorded by a potentiometer and inscribed on the strip chart recorder. To eliminate errors of measurement caused by instability of the power-supply voltage and by electromagnetic noise, a current-stabilized source is used.

Using the horizontal vibration of a rod gives this vibrometer an advantage over similar devices using vertical vibration, because of the more intimate contact of the vibrating tip of the rod with the particles of the material being studied, and a constant contact of the vibrating rod with the material (due to the horizontal travel of the stand), which increases the accuracy of measurement and the sensitivity of the device.

As the process of hardening of a compound proceeds, the amplitude of oscillations of the vibrating rod decreases, and at total hardening it drops to zero. The whole process is recorded on the automatic potentiometer.

¹ a device developed at VNIIST by Yu. N. Alekseev, engineer

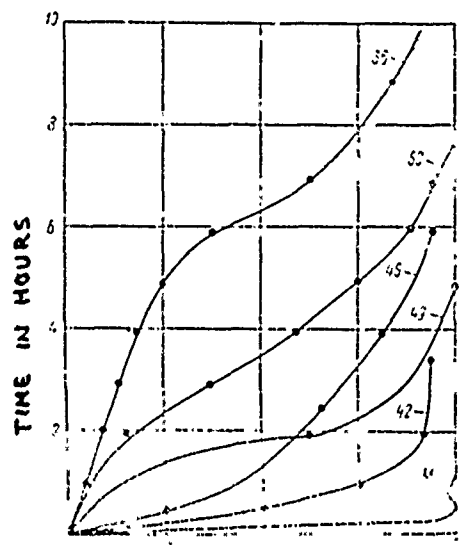


Fig. 42. Curves of hardening. 36, 42, 45, 49, 50 - numbers of compounds; M - rubber-bitumen enamel

The hardening of various compounds is illustrated on graphs obtained at a rate of chart movement of 60 mm/hour (Fig. 42). The hardening curve of a rubber-bitumen enamel is shown for comparison. Specifically, the initial section of the curve indicates cross-linking (gelation) of the mixture; in the zone of total hardening the curve does not change and this part of the curve is taken to be 100% hardening.

Depending on the duration of hardening of the constituents, the required rate of movement of the chart paper on the autorecording potentiometer is selected: the faster the compound hardens, the faster the chart's rate of travel.

Adhesion-cohesion stability is used to determine the stage of hardening of a composition at various temperatures. Stability of bonding of the material to the base layer depends both on the molecular nature of the material itself, and on the nature of the base layer to which it is applied. Little theory is in existence as to the nature and mechanism of adhesion. Some researchers explain the high adhesion of a polymer to metal by chemisorption of the functional groups of the substance; others believe that a strong adhesion coupling is never established between polar and nonpolar substances. Several authors consider the phenomenon of adhesion to a surface a process, the result of which is adsorption of certain parts of molecules adhesive on the surface of the base layer.

A. Staverman and others believe that the phenomenon of adhesion depends to a significant degree on structure and, consequently, on the energy of the surface force as well, and that this phenomenon comes under capillary attraction or repulsion and wetting. The main thing determining the possibility of liquid penetrating into pores of a solid body would then be the surface

tension of the pure liquid on its air boundary, determined by the angle of wetting ϕ between the solid and the liquid. A. Staverman concluded that the polarity of adhering substances and the magnitude of adhesion give only a very general and qualitative idea as to adhesion phenomena and do not make it possible to perform any kind of quantitative computations.

The studies of B. V. Deryagin and N. A. Krotova have shown that the work expended in peeling polymers from a solid base layer is several orders of magnitude less than that required for overcoming the intermolecular forces. Moreover, the work expended in detaching polymers depends on the velocity of detachment and, as is well known, the velocity factor has no effect on the work expended to overcome forces caused by intermolecular interaction.

To explain the essence of adsorption theory, B. V. Deryagin and N. A. Krotova have suggested an electrical theory of adhesion. It is known that a so-called image electrical layer is formed on the interface where solid and liquid bodies are in contact, and that this layer serves as a kind of capacitor. Noting the effect of the image electrical layer in the contact zone on the size of the contacting body, the originators of the electrical theory of adhesion retain the effect of molecular interaction forces and consider that the work expended on overcoming the adhesion bond has two components --the electrical and the molecular. Apparently the effect of electrical and molecular factors will differ, depending on the nature of the contacting body, conditions of peeling, and other factors.

The nature of the adhesion bond in copolymers is described in a diffusion theory of adhesion by V. V. Karasev, S. S. Boyutskiy, et al. According to this theory, adhesion of polymers leads to diffusion of long-chain molecules or of their individual parts, and the consequent formation of a stable bond between the adhesive and the base layer.

Considering the inconsistency and proliferation of theories to explain the adhesion process, it cannot be claimed that only adhesion is determined by means of a given method, since peeling of the insulated layer more often occurs in the material itself, and depends more on its structural stability. The adhesion-cohesion stability of a coating must be determined. Determining the hardening rate of constituents by a change in adhesion-cohesion stability is based on the fact that when synthetic resins are hardened by gelation of constituents of the material, stabilization results from a change in structure. When insulating materials are applied on a well-prepared surface, adherence of the material to the metal surface is increased according to the degree of hardening.

The rate of hardening of coatings is determined in relation to the change of adhesion-cohesion stability in the temperature range from -50 to $+90^{\circ}\text{C}$ (at 10° intervals) by peeling the coating from the metal base layer. The device by means of which the determination is made consists of a hollow truncated cone and a metal disc. The test material is poured into the cone, then hardened and subjected to peeling. Adhesion is determined by the amount of force needed to peel the coating from the metal. Since the rupture almost always occurs in the material and not on the metal-coating boundary, the cohesion stability of the material is exhibited along with its adhesion stability.

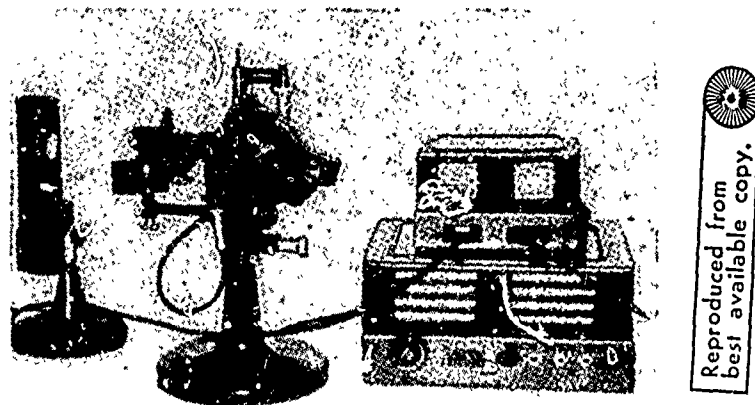


Fig. 43. IPF-23 refractometer with sodium lamp

Adhesion-cohesion stability is ascertained on a tensile strength testing machine, type TSMGIT-250, with a pendulum system. This machine is designed for testing resins and similar materials for elongation and stretching at high and low temperatures, in the temperature range from -60 to $+100^{\circ}\text{C}$. Low temperatures are attained in the environmental chamber by means of a two-stage mechanical refrigeration apparatus, and higher ones by an electrical heater.

Optical methods make it possible to estimate the completeness of hardening of a composition in the hard state; this technique uses change in the coefficient of refraction to determine the rate of hardening (by a refractometer).

When compositions made of synthetic resins harden, a certain shrinkage of the material occurs, as a result of which the density and index of refraction of the composition increase. Change in the coefficient of refraction is the criterion for judging the degree of hardening of a composition.

The rate of hardening is measured on an IPF-23 refractometer designed for determining the index of refraction of liquids and solids in the range from $1.33 - 1.78$ to an accuracy to $1 \cdot 10^{-4}$.

The refractometer consists of measuring prisms (with different coefficients of refraction), a telescope, a reading device and a lighting system (Fig. 43) serving to illuminate the object studied with an oblique beam of light. Two light sources are provided for in the construction of the illuminator: Geissler tubes and a sodium lamp, readily interchangeable during operation.

Measurements are performed one day after the samples are poured, and every third day after that, until the readings are constant.

For each of the compounds a fixed prism is selected whose index of refraction is as much larger as possible than that of the compound, and another prism is chosen to be used with it which has an index of refraction as close as possible to that of the compound to be studied.

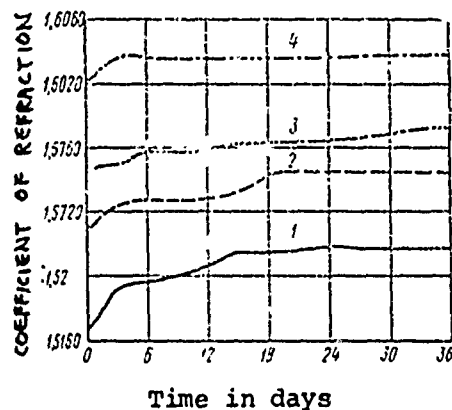


Fig. 44. Dependence on time of hardening of coefficient of refraction of various compositions. 1 - ED-5 - 100 parts by weight, PEPA - 14.5 parts by weight; 2 - ED-6 - 100 parts by weight, PEPA - 12.4 parts by weight; 3 - ED-5 - 100 parts by weight, L-18 (polyamide) - 80 parts by weight; 4 - ED-6 - 100 parts by weight, L-18 - 80 parts by weight.

As an example, Fig. 44 shows dependence curves of the coefficient of refraction of several compositions of different make-up upon the period of hardening, from which it is evident that the coefficient of refraction increases with the duration of time for all compounds.

Hardening time, as determined by various methods for the different compounds, is usually from one to eight hours for the cold method of hardening; however, it takes not less than three days to reach total hardening. The hot method of hardening requires from one to three hours. This method gives a thicker, more waterproof coating, especially with the first time.

With the cold method the hardening process is much slower, and storage and service are included in the process.

CHAPTER FOUR

TECHNIQUES OF PREPARING AND APPLYING COATINGS

Preparing the Pipe Surface Under the Coating

The most important requirement for good adherence of the protective coating to the metal is the preparation of the surface (cleaning it of dust, dirt, corrosion products, greasy spots, moisture).

Mechanical methods of cleaning use sand-blasting devices, cleaning machines, or manual metal brushes. Under factory conditions pipes of all diameters are cleaned mechanically or by chemical means.

Mechanical cleaning of pipe can only be done on a dry pipe surface. After mechanical cleaning the surface of the metal should remain rough. Any deposit of rust flakes settling on the surface of the pipe during the cleaning process should be avoided.

Methods for cleaning surfaces are constantly being improved. The most effective method is shot-blasting of surfaces.

However, mechanical cleaning of pipelines, tanks, bridges, wells, and other structures is inconvenient, laborious, and at times ineffective. In this connection, recent years have seen much attention given to developing chemical methods for cleaning surfaces, specifically, methods of converting corrosion products into a protective layer by means of oxygen, pastes, etc. without removing them from the surface of the objects.

In a majority of cases the protective layer consists of difficultly soluble or practically insoluble compounds of phosphates or chromates, or sometimes oxides or silicates. Anions present in the liquid state and interacting with the metal are converted into insoluble compounds. This reaction occurs at a much faster rate than the rate of diffusion of ions out of the liquid or out of the boundary film. A protective layer is therefore formed directly on the

the metal surface during deposition of an insoluble metal compound. The metallic surface is thus covered by an insoluble metal compound.

Such coatings are often called conversion coatings. In their process of formation, the growth of the protective film is complete when a large portion of the corrodable surface metal has been transformed into insoluble compounds.

Inorganic conversion coatings are thin and porous. But despite the high porosity, phosphate films can nevertheless protect metals from corrosion for a certain time.

Additional coatings of resins, lacquers or paints provide durability of the protective phosphate film. The porosity of the protective layer promotes stable bonding of the organic coating to the surface of the metal.

Protective films are formed on fixed structures:

- by cleaning the surface with a dilute solution of phosphoric acid;
- by applying pastes made from iron phosphate;
- by rustproofing or thin-layer priming, etc.

Treating a corroded surface with a solution of dilute phosphoric acid is the most prevalent method of cleaning. To provide simultaneous degreasing, the solution contains some organic solvent, for example butyl alcohol, and surface-active substances. The compound is sprayed or brushed on.

Other conversion agents which are of interest are those which are products of steel corrosion, which lead to the formation of iron phosphates on the metal, a coating of rust or scale.

Rust conversion agents often consist of a concentrated solution of phosphoric acid with small admixtures of wetting agents, accelerators and metal phosphates. Their purpose is to combine rust and scale removal, degreasing, and the rustproofing process in one operation, without preliminary pickling. Various thickening agents are often introduced into the phosphate solution; various resins are used for this. In this case the rust conversion agent is applied on a metallic surface in the form of a primer layer.

A rust conversion agent developed in England under the brand name of Kurst is a mixture of phosphoric acid, synthetic resin and lead powder. When it is applied on a workable surface, oxides of iron are transformed into iron phosphate, which forms a continuous film by interacting with other constituents of the compound. The film is thermally stable and water-repellent, and has good adhesion and resistance to solvents, and can serve as a primer under a paint and varnish coating. Kurst compound neutralizes the layer of rust to a depth of 25 microns; if the layer is thicker, then the surface is cleaned with brushes.

The preventive possibilities of rust formation during phosphoric acid processing are more effective. The concentration of phosphoric acid depends on the thickness of the rust layer. Too high an amount can cause excessive release of water, and formation of cracks and blisters in the protective layer. Increasing the corrosion inhibitors limits the action of the phosphoric

acid on the metallic base. Sometimes accelerators are introduced into the formulation of the conversion agent to boost the reaction between surplus phosphoric acid and the metal to such a degree that it occurs right up until hardening of the protective layer. A compound based on polyvinylbutyral, on a base of zinc chromate and phosphoric acid, is used as an inhibitor for the base layer. The compound is applied to steel which has tightly adhering scale and patches of rust. During processing with compounds based on phosphoric acid (especially those with a high content of it) a thin layer of rust can be converted into insoluble phosphates.

Several types of conversion agents are used in the USSR: No. 1 - based on tannin, No. 2 - based on tannic extract of oak, No. 3 - based on syntan.

A conversion agent for corrosion products based on yellow potassium ferrocyanide and orthophosphoric acid (No. 4) is presently in quite general use. ED-5 or ED-6 resins can also be part of the formulation of the conversion agent, in the form of suspensions in toluol. Two primers are then applied to the surface, the first consisting of yellow potassium ferrocyanide and orthophosphoric acid, and the second of epoxy resin; to improve the quality of the coating red potassium ferricyanide is introduced into the composition of the first primer, and furfural acetone FA monomer into the composition of the second. The epoxy resin and FA are introduced to bond the residues of acid, which is used as a hardener for the FA monomer.

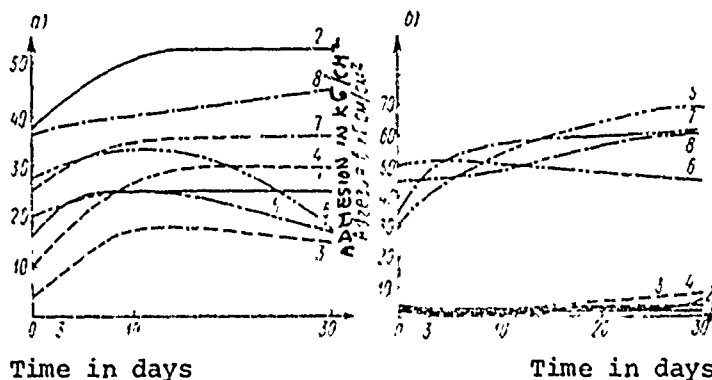
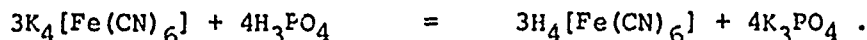
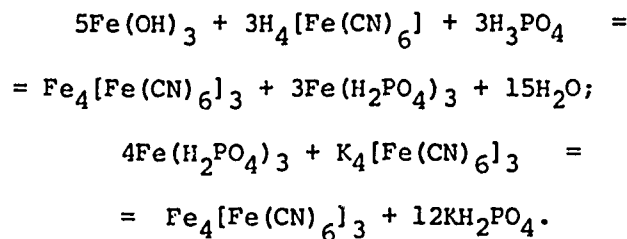


Fig. 45. Adhesion-cohesion stability of coatings applied on a steel surface treated with corrosion product conversion agents. a - compound 45; b - compound 89; 1, 3, 5, 7 - conversion agents No. 1, 2, 3, 4, applied on a dry surface; 2, 4, 6, 8 - same on a moist surface

The following reaction occurs during preparation of the mixture of orthophosphoric acid and yellow potassium ferrocyanide:



When the mixture is applied on a rusted surface, corrosion products are converted into compounds of iron and phosphates:



However, as several authors have noted, the surface layer formed is rather brittle and badly bonded adhesively with the structural metal.

To prepare the conversion agent based on yellow potassium ferrocyanide, 160 grams of 80% orthophosphoric acid and 20 grams of yellow potassium ferrocyanide are carefully mixed to obtain a white, homogeneous mass.

The conversion agents are painted or smeared onto the metal surface, which has been cleansed of grease, deposits or other easily flaked rust. The coating is applied on the metal surface (the thickness closely bonded with the metal of the rust should not exceed 100 - 150 microns) a day after the conversion agent has been applied. Experiments show the coating's impact resistance is such as to sustain impacts from 40 to 85 kg · cm/cm² or more. Fig. 45 shows the adhesion-cohesion stability of the coatings.

Preparation and Application of Bitumen Coatings

Polymer-bitumen or rubber-bitumen enamels are used as the basic layer protecting steel pipelines from soil corrosion, and as a bonding layer in the application of roofing wrapping materials.

Factory-made rubber-bitumen enamel enters the production line in paper sacks weighing 45 - 50 kg and is fused in traveling bitumen tanks. Before going into the tank, each sack of enamel is broken into not less than eight pieces. The weight of the enamel chunks must not exceed 7 - 8 kg. The smallest chunks of enamel are loaded into the bottom of the tank. To avoid charring of refractory enamels (types MBR-IL-90 or MBR-ILT-100) as they are fused, BN-IV bitumen, in a quantity of 10% of the weight of the enamel to be loaded, is loaded into the bottom of the tank for the first heating cycle. The loading of the tank is calculated so that the volume of the melted mass will occupy not more than two thirds of the capacity of the tank. Pieces of paper adhering to the chunks of mastic are removed from the melted mass by a special sieve.

The period needed to fuse rubber-bitumen enamel in the tank at 180 - 200°C is three hours. If the enamel is very moist, it is heated until completely dessicated. The enamel must be stirred around during melting so that it does not get superheated around the fire tube or the wall of the tank.

After withdrawal of the enamel from the bitumen-melting tank, one quarter of the volume of the tank is still filled with melted enamel, which provides more rapid and uniform fusing of the next batch of enamel. After each shift,

the tank must be cleaned. The process is considerably simplified if the rubber-bitumen enamel arrives at the production line in briquets.

Rubber-bitumen enamel of this same composition is prepared at the construction site in the following manner: type IV or V bitumen delivered from a petroleum refinery in the hard state in paper sacks is broken up into chunks weighing not more than 7 kg. The bitumen is dessicated and mixed with pulverized rubber (VTU No. SHU-96-56) at 160 - 180°C.

The mixture is stirred with a pump-mixer or plate and frame mixer, stirring rod, or other mechanical means in field-type tanks. The melting and dessication of the bitumen, as well as maintenance of the temperature in the range from 160 to 180°C necessary to prepare the enamel, are accomplished by heating the contents of the tank externally by electrical or open flame means.

The surface of the pipe is covered with a primer before the enamel is applied. The primer, prepared from one part of bitumen and two parts of aviation or auto gasoline, must be applied on a dry surface, immediately after cleaning, in an even layer without skips, blobs, or underfilm leakage.

The insulating enamel is applied on top of the dry primer, which should no longer be sticky to the touch. Insulating enamel cannot be applied on moist pipe surfaces, or during rain, fog or strong wind. Insulating coatings can be applied by any method providing the requisite thickness and integrity of the insulating layer.

When the coating is applied at an ambient temperature below 30°C the temperature of the bitumen enamel is raised from 160 to 190°C; at ambient temperatures above 30°C the enamel temperature may be dropped to 150°C.

Fiberglas and brizol are applied on top of the hot enamel with a 2 - 3 cm overlap. The wrapping should lie smoothly against the coating without blisters, wrinkles or creases. During application on the pipe, the material used to cover it should be dry and uncontaminated.

Application of Coatings Made From Synthetic Resins

The technological process of applying coatings made of synthetic resins has its own special problems.

The basic advantage of coatings made of synthetic resins lies in their high protective properties and durability, and also their ability to provide a sufficiently thick layer (0.5 - 1 mm) with only a single application. Moreover, the absence of solvents in the compounds gives them greater density and integrity and lowers the shrinkage of the material, i.e. the drawback, which are natural to bitumens, and especially paint and varnish coatings, are overcome.

However, the rather high viscosity of compounds made from synthetic resins creates certain difficulties in devising techniques and equipment for their application. Another problem with these compounds is their limited period of

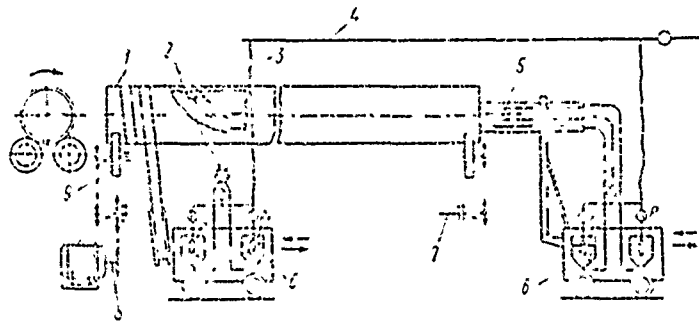


Fig. 46. Basic flow sheet for applying insulations made out of synthetic resins, using traveling trolleys and rotation of the pipe on rollers. 1 - pipe; 2 - sprayer; 3 - flexible hose; 4 - air line; 5 - internal hose; 6 - traveling trolley; 7 - drive shaft; 8 - electric drive; 9 - supporting rollers.

usability. Epoxy compounds can be used for 45 - 60 minutes after they are prepared; after that the compounds gel and become unsuitable for use. The third problem with such coatings is the hardening of the compound used, which, as has already been mentioned, can be by either the hot or the cold method.

Thus the following mode of preparation of these compounds is presently in use: the composition is divided into two parts, which are mixed in two mixers, epoxy resin and part of the filler M_1 in one, and the remaining constituents and hardener M_2 in the other. This separation eliminates premature hardening of epoxy resin coatings. For application the two streams of ingredients are mixed in and sprayed from a specially developed pistol-type sprayer or a mixer-sprayer. Using the hot method for hardening and a temperature of 80 - 90°C, they are done over the course of 3 - 4 hours. The cold method is more efficient. It is done at a temperature not lower than 18 - 20°C; at lower temperatures ingredients M_1 and M_2 are heated to 40 - 60°C, which provides the required temperature during contact with the metal. The basic stage of hardening --gelation-- occurs within 2 - 3 hours. When accelerators are used, the hardening time is cut to 30 - 60 minutes. The pipes are ready for shipping after 24 hours.

Each hardening method has its own advantages and disadvantages. Advantages of the hot method include shortness of the production and application cycle, and improvement of the physical and mechanical properties of the compounds, for example, adhesion. However, this method involves significant losses of energy, as well as complicated equipment. Among the advantages of the cold method of hardening are ease of application, heightened protective properties, and lengthened service life of the coatings.

An industrial-type apparatus (Fig. 46) has been designed to implement the technique for applying epoxy-coal-resin coatings on the external and internal surfaces of pipes and overcome all the technical problems involved. This apparatus makes it possible to apply insulation on pipe with a diameter of 325 - 1220 mm and a length of 6 meters by the spray method.

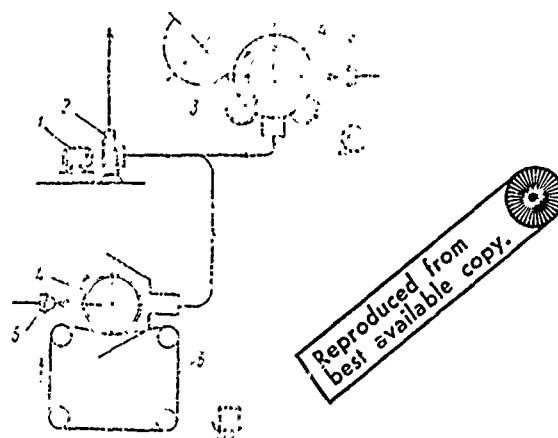


Fig. 47. Diagram of ventilation system. 1 - electric motor; 2 - ventilator; 3 - supporting rollers; 4 - pipe to be insulated; 5 - sprayer; 6 - conveyor device.

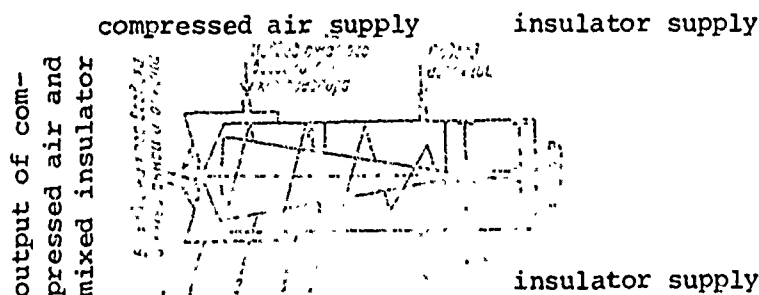


Fig. 48. Main diagram of screw-conveyor sprayer-mixer. 1 - nozzle; 2 - cone-shaped endless screw; 3 - body of mixer-extruder; 4 - mixing paddles.

The device consists of a rotator which imparts rotational movement to the pipe as the coating is applied and during the gelation process, a traveling pulley with small tanks for ingredients M_1 and M_2 , a sprayer, and a ventilation device (Fig. 47), which is a duct with low suction, located under the pipe.

A lift mechanism feeds the pipe onto a rolling mill. The insulating material is applied to the pipe by means of a pneumatic sprayer, which allows two high-viscosity liquids to be mixed and sprayed out in one jet. The material is propelled into the sprayer from two small tanks by means of compressed air.

The sprayer and small tanks are positioned on a trolley whose movement along the pipe is automatic. The pipe continues to rotate after application of the compound, until total gelation (cold hardening) on the rolling mill. The rolling mill can rotate three to four pipes simultaneously.

Fig. 48 shows the main parts of the screw-conveyor sprayer-mixer for applying high-viscosity compositions on the external surfaces of pipes.

The constituents of the compounds are fed into the body of the mixer-extruder through orifices and are taken up by the conical screw by the sweep of the paddles against the screw thread, and are thus transported to the output nozzle of the sprayer. The ingredients are partially mixed in transit by means of the paddles, and at the output orifice they are taken up by the air current coming from the nozzle, where they are finally mixed, after which they strike the pipe surface. The conical screw is mounted on ball thrust bearings. The mixer-sprayer has been tested in operation and showed good results.

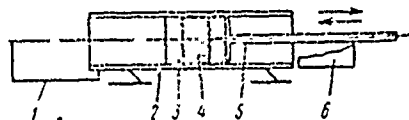


Fig. 49. Flow sheet of application of insulation on internal surface of pipe. 1 - catch pan; 2 - pipe; 3 - piston; 4 - insulating material; 5 - bar-plunger; 6 - guiding device.

RELATIONSHIP OF SI UNITS TO UNITS OF OTHER SYSTEMS

Property	Units of measurement		Coefficients translated into SI units
	Other systems	SI	
Coefficient of viscosity:			
dynamic	pz	$\text{n} \cdot \text{sec}/\text{m}^2$	$1 \text{ pz} = 0.1 \text{ n} \cdot \text{sec}/\text{m}^2$
kinematic	st	m^2/sec	$1 \text{ st} = 10^{-4} \text{ m}^2/\text{sec}$
Viscosity:			
specific	$\text{kg} \cdot \text{cm}/\text{cm}^2$	joule/m^2	$1 \text{ kg} \cdot \text{cm}/\text{cm}^2 = 9.81 \cdot 10^2 \text{ j}/\text{m}^2$
impact	"	"	"
Pressure, stress, mechanical (limit of resistance in elongation, bending, shrinkage)	kg/m^2	n/m^2	$1 \text{ kg}/\text{m}^2 = 9.81 \text{ n}/\text{m}^2$
Density	g/cm^3	kg/m^3	
Breakdown voltage	kv/mm	v/m	$1 \text{ kv}/\text{mm} = 10^6 \text{ v}/\text{m}$
Specific heat	$\text{cal}/\text{g} \cdot \text{degree}$	$\text{j}/\text{kg} \cdot \text{degree}$	$1 \text{ cal}/\text{g} \cdot \text{degree} = 4.1868 \times 10^3 \text{ j}/\text{kg} \cdot \text{degree}$
Coefficient of thermal conductivity	$\text{kcal}/\text{m} \cdot \text{hour} \cdot ^\circ\text{C}$	$\text{vt}/\text{m} \cdot \text{degree}$	$1 \text{ kcal}/\text{m} \cdot \text{hour} \cdot \text{degree} = 1.163 \text{ vt}/\text{m} \cdot \text{degree}$
Brinell hardness	kg/mm^2	n/m^2	$1 \text{ kg}/\text{mm}^2 = 9.81 \text{ n}/\text{m}^2$
Modulus of resilience	kg/cm^2	n/m^2	$1 \text{ kg}/\text{cm}^2 = 9.81 \cdot 10^4 \text{ n}/\text{m}^2$
Resistivity:			
specific volume	$\text{ohm} \cdot \text{cm}$	$\text{ohm} \cdot \text{m}$	$1 \text{ ohm} \cdot \text{cm} = 0.01 \text{ ohm} \cdot \text{m}$

Insulation is applied to the internal surface of the pipe with a sprayer set on a bar, which is propelled inside the pipe by means of the traveling trolley. The mixes are dropped from the small tanks along the hose mounted on the internal bar. On the internal surface of the pipes the insulation is applied, also, by means of a pneumatically driven piston. Fig. 49 shows a flow sheet of application of insulation to the internal surface of a pipe.

The equipment for applying insulating coatings made of synthetic resins solves the technological difficulties associated with problems of applying high-viscosity coatings.

The use of the principle of separate feeding of ingredients into the sprayer or the sprayer-mixer eliminates the danger of premature hardening of a compound in the system, and takes care of the matter of poor viability of epoxy compounds.

To provide the correct proportions (in accordance with the formula) the viscosity of the two compounds should be identical at the output orifice of the sprayer. The most easily handled is a viscosity of $28 \cdot 10^3$ centipoise.

The proportions of the ingredients of the compound to be sprayed onto the pipe are regulated by viscosity, pressure, or pump feed of the mass. Special measuring devices make it possible to measure constituents of the compound more accurately.

To obtain an insulation layer of the specified thickness of 0.5 - 1 mm, the rate of travel of a sprayer along the pipe should be 1 m/min; the rate of rotation of the pipe 16 rpm; pressure in the small tanks 4.5 - 5 atmospheres; temperature of aid supplied into the tanks and sprayer around 30°C; viscosity of the mixture at 18 - 20°C, 45 sec on the VZ-4 scale (or 10^3 - 10^4 centipoise). It takes six minutes to insulate a pipe 6 meters long with one sprayer.

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